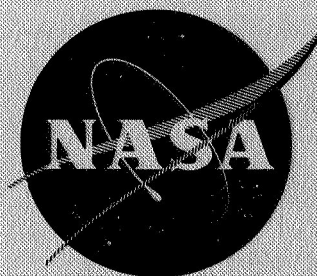


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FINAL REPORT
For the period
1 May 1966 to 2 July 1967

VOLUME II - LITERATURE REVIEW OF
ADSORPTION ON METAL SURFACES

By

L. W. Swanson
A. E. Bell
C. H. Hinrichs
L. C. Crouser
B. E. Evans

27 July 1967

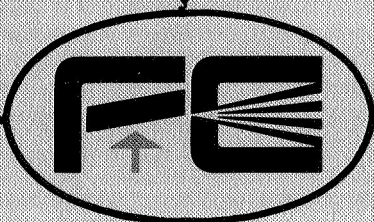
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Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Electric Propulsion Office



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Field Emission Corporation

McMinnville, Oregon

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Melrose Avenue at Linke Street
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LIST OF SYMBOLS - PART I

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
α	polarizability of adsorbate	16, 17, 5, 7, 10, 12, 13
α_a	polarizability of adatoms	14
α_i	polarizability of adions	14
$ a\rangle$	configuration representing system without interaction between its parts	2
α, β	correlation dependent terms	20
$ \beta\rangle$	configuration derived out of $ a\rangle$ by electron transitions	2
2β	angle between the direction along R for two diagonally opposite pairs of substrate, adsorbate atoms arranged in a square lattice	17
δ	distance travelled by adparticle before evaporating	13
δ_o	distance between nearest atoms in substrate	13
Δ	extent of band broadening	14, 10, 20
δ	= 1 for mobile adsorption = $\theta^{-1/2}$ for immobile adsorption	15
δ	$F_q(e^2/r - V_I)/\phi$	6
ϵ	dielectric constant	7, 17
η	$d_{cf} d_{cc}$	1
η_r	$d_{cf} d_{ff}$	1
η	equal to $N\Delta V_a(1)/V_a(1)$	21
\textcircled{H}	angle between outward normal to surface through ion and radius vector joining the ion and the surface element through it	7

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
θ_a, θ_i	relative coverage of atoms and ions	9, 14
λ	dimensionless parameter	3
μ	radial linear momentum	20
ν	semi-empirical constant	7
ν_i	quantum number	19
π	state such that $z > 1$	1
Π	spreading pressure	13
ρ	density of electrons per unit volume in the metal	12
$\rho_{kl} \rho(E)$	density of states in the metal	19, 20
$\rho_i(Z)$	charge distribution of ion cores within the metal	19
σ	surface coverage in atoms per unit area	13
σ_o	number of adsorption sites	5, 7, 8, 14, 17
τ	lifetime of an adsorbed molecule	13
τ	$V_a(1)/V_{ai_1}(1)$	21
ϕ	molecular wave functions	12
ϕ	work function of substrate plus adsorbed layer	17, 18 7, 8, 6, 14,
$\Delta\phi$	work function change due to adsorption	15, 17, 7 8, 9, 10
ϕ_m	clean substrate work function	13, 14, 17
χ	constant depending on crystal structures	8

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
χ	metal wave function	12, 20
χ_M, χ_A	electronegativity of M and A	8
χ_F	electronegativity of adsorbate/substrate complex	17
χ_S	magnetic susceptibility per gram atom	11
ψ	single electron wave function	1, 3, 11 18, 20
Ψ	total system wavefunction	11, 20
$\psi_{n,s}$	wavefunction of alkali metal s electron	19
ψ_I	wavefunction of system of adsorbed particles and crystal	4
ψ_k	wavefunction of undisturbed crystal	4
$\psi_{\bar{n}}$	wave function of system of adsorbed particles, no account being taken of interaction with crystal	4
ψ_{Mg}	wave function of adsorption complex	4
ψ_D	wavefunction of dative state	5
ψ_{NB}	wave function of no-bond state	5
ψ_o, ψ_m	wavefunctions of the system of molecule plus metal in the initial and final state respectively	12
$\psi_{m,k}$	metal wave function	19
Ω	number of crystal atoms	1
ω_i	$= E_i - E_o$	2
Ω	constant ≈ 9	15

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
A	$\ln \left[\cos \left(\frac{H}{H_c} \right) \right]$ where $\left(\frac{H}{H_c} \right)$ is the maximum value of $\left(\frac{H}{H_c} \right)$	7
A	theoretical Richardson's constant	13
b	\sim a measure of adsorption energy	13
c	$4\pi\sigma_o / r_i$	7, 8
c_i^2	fraction of ionic character of bond	8
c	velocity of light	11
c_1, c_2, c_3	constants	13
d	nearest neighbor distance in adsorbed array	10, 16, 21
d_1	nearest neighbor distance in adsorbed array when $\theta = 1$	7, 8
D	dielectric displacement	7
$d(\theta)$	dipole barrier	17
$e(\theta)$	electronegativity barrier	17
E_n	total electron energy of a chain of n identical atoms	1
E_{n+1}	total electron energy of a chain of n identical atoms with a foreign atom added	1
E_o	energy of system without interaction between its parts	2
E_1, E_2, E_3	energy of configurations $\beta_1, \beta_2, \beta_3$, etc.	2
E_f	Fermi energy level	2
E_d	dispersion energy	5
E_π	energy of ethylene bonding level	2

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
E_{π}^*	energy of ethylene antibonding level	2
E_{sur}	energy solution of secular equation	3, 8
E_{oA}	energy level of adsorbing atom in free state	3
E_{o}	energy level of lattice atom in free state	3
E_{I}	energy of whole system	4
E_{k}	energy corresponding to wavefunction of undisturbed crystal	4
E_{o}	energy corresponding to isolated adsorbate atoms	4
$E_{\text{k}, \text{o}}$	zero coverage heat of adsorption	4
E_{s}	heat of formation of surface complex	5
$E_{\text{a}}, E_{\text{p}}$	total heat of adsorption	5, 11, 12
$E_{\text{a}}, E_{\text{p}}$	atom and ion desorption energies	6, 9, 14
$E_{\text{ao}}, E_{\text{po}}$	values of E_{a} and E_{p} when $\theta \rightarrow 0$	6, 9, 14
$E_{\text{f}}, E_{\text{m}}$	heat of sublimation of the adsorbate and metal	6
\bar{E}_{f}	field energy of the adsorbed layer per unit area	7
E_{f}	field energy created by the adsorption of one ion on the surface with coverage θ	7
E_{i}	energy due to attractive force between an ion and the image charges of its neighboring ions	7
$E(\text{M-M})$	bond energies of the single bond M-M	8

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
$E(A-A)$	bond energies of the single bond A-A	8
E_o, E_m	energies corresponding to the state ψ_o, ψ_m	12
E_j	energy of the jth state of the molecule	12
$\Delta E, \Delta E_o$	energy difference between adsorbed ions and atoms at coverage θ and when $\theta = 0$	14
ΔE_a	equal to $E_a - E_{ao}$	14
E_u	energy of shifted valence level	20
E_H	one electron Hartree energy	20
E_t	total system energy	20, 21
E_A	electron affinity of adsorbate	5, 8
E_R	rearrangement work	21
ΔE_p	energy required to remove an adion from its equilibrium position minus that when $\theta = 0$	10
F	electric field, depolarizing field in paper 14	5, 7, 20
F_1	self-consistent effective field leading to induced polarization	15, 16
F_2	self-consistent effective field leading to induced polarization perpendicular to adsorbent surface	10, 15, 16
F_{n1}	effective field leading to induced polarization of a single isolated adsorbed element in the absence of average charge on the adsorbent	15
F_{n2}	effective field orienting a single isolated adsorbed dipolar element in the absence of average charge on the adsorbent	15

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
F_{eff}	$4\pi q + F_d$	15, 16
F_d	self-consistent, time average depolarizing field	15, 16
f, f_m, f_{im}	ion array penetration parameters in general, for mobile arrays of adions and for immobile arrays	9, 10, 14
f_1, f_1^0	least accurate value of f , and corresponding value when $\alpha = 0$.	10
f_2	correct value of f when rearrangement work is neglected	10, 21
f_3	correct value of f when rearrangement work is included	10
F_q	fraction of charge of the adsorbate which is transferred to the substrate	6
$G(E_i)$	density of configuration with energy E_i	2
$g(E)$	density of states of conduction electrons in the metal	2
$G(\theta)$	polynomial $1 - 3\theta^2 + 2\theta^3$	17
$H_{\text{ii}}, H_{\text{cc}}$	ionic and covalent contributions to the bond energy	6, 8
ΔH_o	desorption heat for $\theta \rightarrow 0$	7, 8
h_o, h_a	heat of vaporization of substrate and bulk adsorbate	8, 14
H	Hamiltonian	2, 5
H	self-consistent Hamiltonian for an electron	20
H_{tot}	Hamiltonian for total system	19

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
H_m	Hamiltonian for unperturbed metal	19
H_a	Hamiltonian for unperturbed adsorbate atom	19
H_{int}	Hamiltonian for coupling between metal and adsorbate atom	19
H'_{a-m}	perturbation effect of metal on the alkali metal electron	19
H'_{m-a}	perturbing effect of alkali ion core on metal electron	19
H_A	$= T_O + V'_A$	20
h	Plank's constant	14
L_i	angular momentum perpendicular to surface	19
I	coulomb integral	1, 3
I_c	coulomb integral of atom in chain	1, 3
I_e	coulomb integral of end atom in chain	1, 3
I_f	coulomb integral of adsorbed or foreign atom	1, 3
I_{cc}	resonance integral between atoms in chain	1, 2, 3
I_{cf}	resonance integral between end atom and adsorbed or foreign atom	1, 3, 5
I_{ff}	resonance integral between two adsorbed foreign atoms	1
j	number of localized energy levels in valence band	14
k_m	momentum quantum number	12
K	constant of proportionality between dipole moment and electronegativity differences	17

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
L	Avogadro's number	11
L_c	lattice constant	9
L_{fm}	angular efficiency of orbitals	6
l	integral which is a function of M, T, and θ	13
L	length of cubic metal crystal	19
M	dipole moment	5, 8, 11, 12, 13
M_{oj}	equal to $\int \phi_o^* M \phi_j d\tau$ where ϕ 's are molecular wave functions	12
M_i	dipole moment of ion-substrate complex	14
M_a	dipole moment of atom-substrate complex	14
M_{io}, M_{ao}	limiting values of M_i and M_a as $\theta \rightarrow 0$	14
$\langle M(F_2^x) \rangle$	time average value of normal component of permanent dipole when orienting field is F_2	15, 16
M_o	value of dipole when $\theta \rightarrow 0$	17, 19
M_e	effective dipole reduced by depolarization	17
M_{fm}	perpendicular component of the dipole moment formed between an adsorbate atom and each of its four nearest neighbors	17
$N_e(\mu E)$	density of metallic states with angular momentum l per unit radial momentum	20
n	number of nearest neighbors	4
N_v	largest number of electrons that can participate in a bond	6

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
n	effective valence of adions	10, 15, 16, 21
n^*	an effective quantum number	20
N	number of atoms in chain	1
N	adsorbate surface density	10, 21
N_s	maximum adsorbate surface density	15, 16
n_o	number of electrons in metal	19
n_r	index of refraction of bulk adsorbate	15
P_1	average induced polarization in layer of thickness t	15, 16
P_2	average permanent dipole polarization in layer of thickness t	15
ρ	state such that $z < 1$	1
$P_{id}(\theta)$	probability that an adsorbate ion exists at a lattice site ij in a square array	1
P	pressure	13
$q_d(\theta)$	differential heat of adsorption	4
$q_d(0)$	value of $q_d(\theta)$ as $\theta \rightarrow 0$	4
q	electrode surface charge density	21
q_a	surface charge density on adsorption plane	15, 21
q_a	atom evaporation rate	13
q_p	ion evaporation rate	13
q	evaporation rate	13

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
q	effective charge in volume V around the atom	20
q^-	electron charge around alkali ion core	20
q_f, q_m	valence charge of the adsorbate and metal	6
Q_{fm}	charge efficiency	6
r	distance of nucleus of adsorbed particle from surface	2, 5, 10, 15 16, 19, 9, 21
R	sum of adsorbate and substrate covalent radii	6, 8, 17
\textcircled{r}	length of radius vector	7
r_i	radius of adsorbed ion	7, 8, 14
r_i	position vector of electron	20
R_1	equal to d/r	10, 16, 21
r_3	distance between test charge and image plane	9
r_e	distance between molecule and eth electron	12
r_n	distance between molecule and nth positive charge	12
r_{c-c}	carbon-carbon distance in ethylene	2
r_{ij}^+	distance between ion at z from the surface and an adsorbed ion at a site on the surface at ij	9
r_{ij}^-	distance between ion at z from the surface and image of ion at site ij	9
r_o	radius of colinear circular vacancies in uniform charge sheet	10
r_{em}	distance between electron and metal	19

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
r_{ei}	distance between electron and image of positive ion	19
r_{ep}	distance between electron and adsorbate ion	19
R_d	Rydberg constant	20
S	overlap integral	5
S_f, S_m	angular strength of adsorbate and metal orbitals used in bonding	6
s_1	constant = 11.03	10, 16
s	condensation coefficient	13
s_z	shielding constant	20,
t	thickness of adsorbed array	15, 16
T_o	kinetic energy operator	20
T	temperature	13, 20
T_m	mean temperature	13
T_{ik}	transition matrix element	19
Δt	lifetime of an adsorbed atomic state	19
μ	ratio of volumes bounded by the Fermi surface and the surface of the nearest brillouin zone	4
u_i	single free-electron eigenfunction	19
u	an atomic s-like wavefunction	20
V_I	ionization potential	1, 5, 6, 7, 8, 13, 14, 18, 20
V_p	potential energy of perturbation	2

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
V_1	potential energy of undisturbed crystal	4
V_2	potential energy of system of particles, no account being taken of interaction with crystal	4
V_o	equal to $4\pi\sigma_o e r_i$	7
$V(Z)$	potential energy of an ion at a distance z along the outward normal to a surface, existing as a result of all other ions in array	9
V_{im}, V_m	evaluation of $V(Z)$ above at point $z = r$ for immobile and mobile adsorption situations	9
ΔV	effective potential increase due to thermal depolarization of ions	9
V_∞	average potential for $Z \gg 1$ arising from adion image array	9, 10, 16, 21
V_a	potential analogous to V_{aic} below but per- taining to a lattice with a single vacancy	10, 21
V_a^o	value of V_a when $a = 0$	10
V_d	potential at the missing adion site arising from the image of the induced dipole of the test ion	10
V_{do}	value of V_d when $\theta \rightarrow 0$	10
ΔV_i	change in value of V_i due to adsorption of one ion	10
ΔV_e	equal to $V_a + 1/2 [V_d - V_{do}]$	10
V_{ap}	potential contribution due to the induced dipole image array (less the dipole at the central image position)	10
v	mutual potential energy of the surface of dipole	12

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
V	potential energy of interaction	12
V_{om}	$\int \psi_{om}^* V \psi_{mo} d\tau$, V defined above	12
V_{∞}^0	value of V_{∞} when $\alpha = 0$	16
V_B	position of bottom of metallic conduction band	20
V_M	potential due to metal ions	20
V_A	potential of the adsorbate ion	20
V_F	potential due to an external field	20
V_{ee}	self-consistent potential acting on one electron	20
V'_A	potential due to adsorbate in modified field by the effective charge q^- in its neighborhood	20
V_{aic}	potential arising from complete adion image array	21
V_e	potential contribution from excess charge on the electrode	21
V_{ic}	equal to $V_e + V_{aic}$	21
V_{iz}	potential due to image of a charge at 0, 0, Z	21
V	equal to $V_a + V_e$	21
V_i	equal to $V + V_{iz}$	21
V_1	$V(1) - V(Z)$ where term in parenthesis denotes Z coordinate at which V was evaluated	21
V_{il}	$V_i(1) - V_i(Z)$	21
V_2	$V(1) - V(\infty)$	21

LIST OF SYMBOLS (cont'd)

<u>Symbol</u>	<u>Meaning</u>	<u>Paper</u>
V_{i2}	$V_i(1) - V_i(\infty)$	21
V_{ai}	$V_a + V_{iz}$	21
V_{ail}	$V_a + V_{il}$	21
x, y	components of complex variable	2
x_r	coordinates of an adparticle electron	11
x_s	coordinates of the image of an adsorbed particle electron	11
X, Y, Z	cartesian coordinate quantities divided by r	21
y	pre-exponential factor	14
Z	the perpendicular distance of an adparticle from the surface	11, 12, 20
Z	$(d_c - d_e)/d_{cc}$	1
Z_r	$(d_c - d_f)/d_{cc}$	1
Z_e	centroid of electron distribution	19
Z_p	centroid of positive ion	19
Z_r	nuclear charge number	11

LIST OF SYMBOLS - PART II

<u>Symbol</u>	<u>Meaning</u>
a_m	average lateral separation of adatoms
b	constant
B	proportional to emitting area
D_o	diffusivity constant
D_F	field dependent diffusion coefficient
d	dipole separation
d_o	dipole separation at monolayer coverage
ez	positive charge per dipole
e	electronic charge
ez_o	positive charge per dipole at monolayer coverage
E_μ	field dipole interaction
E_a	polarization term
E_d^F	field dependent activation energy of surface diffusion
E_d^o, E_d^o	activation energy for surface diffusion without applied field
ΔE	$H(\sigma_t) - H(\sigma_s)$
E_p^F	field desorption energy with positive fields (ions)
E_a^o, E_a	zero field desorption energy for neutral atoms
F	applied field strength
F_o	effective field at the adsorbate
F_s	effective field at Schottky saddle (x_s)

LIST OF SYMBOLS, PART II (cont'd)

<u>Symbol</u>	<u>Meaning</u>
F_t	effective field at trough
F_m	field corresponding to maximum activation energy
g	constant of 2 or 4
H^+	electrostatic surface forces
H^n	nonelectrostatic surface forces
H_d^n	nonelectrostatic surface force contribution from polarization and dispersion binding
H_m^n	nonelectrostatic surface force contribution from metallic binding
H_c^n	nonelectrostatic surface force contribution from covalent bonding
H_a	sum of electrostatic and nonelectrostatic forces involved in bonding
H_a^*	activated state of H_a
$H(\sigma_t), H(\sigma_s)$	coverage dependent zero field heats of adsorption
I_a	adsorbate ionization potential
I	field emission electron current
k_1, k_2	constants
k	Boltzman's constant
k_p	rate constant for field desorption
k_t	F_t/F
k_s	F_s/F
$\ln A$	intercept of Fowler-Nordheim plot
$\ln A_s$	intercept of Fowler-Nordheim plot for clean substrate

LIST OF SYMBOLS, PART II (cont'd)

<u>Symbol</u>	<u>Meaning</u>
r^+	ionic radii
r_o	atomic radii
r_a	adsorbate atomic radii
s	function involving transition probabilities and/or entropy effects
$t(\phi, F)$ $v(\phi, F)$	tabulated non-dimensional functions in the Fowler-Nordheim equation
T	temperature
U	conduction band width
$V(x)$	shift of the broadened valence level in the adsorbed state
x	distance of adsorbate atom from substrate atom
x_s	position of Schottky saddle at s in Figure 4
x_o	equilibrium position of adsorbed atom
x/t	distance traversed by adsorbate atom in time t
x_c	distance of adsorbate atom from substrate atom at point c in Figure 4
y	lateral distance between adatoms
z_m	number of charges per dipole of adsorbate
α	adsorbate polarizability
α_a	polarizability of atomic state
α_i	polarizability of ionic state
Γ	half width of the adsorbate level

LIST OF SYMBOLS, PART II (cont'd)

<u>Symbol</u>	<u>Meaning</u>
ϵ	angle between μ and F
θ	fractional monolayer coverage
μ	dipole moment
μ_o	dipole moment at monolayer coverage
ν	frequency factor
σ_m	adsorbate atom density
σ_o	adsorbate atom density at monolayer coverage
σ_t	adsorbate atom density at emitter tip
σ_s	adsorbate atom density at emitter shank
ϕ	work function
ϕ_s	substrate work function
ϕ_m	minimum work function
$\Delta\phi_m$	maximum work function change $\phi - \phi_s$
ϕ_o	adsorbate work function at monolayer coverage
ϕ_F	field induced work function
$\phi(\sigma)$	coverage dependent work function
$\Delta\phi_c^F$	field induced work function change at x_c
ϕ_c	work function at x_c

PART I - LITERATURE REVIEW OF THEORETICAL MODELS OF WORK FUNCTION CHANGE AND BINDING OF ADSORBED LAYERS

INTRODUCTION

The objective of this work is to provide a review of existing theoretical models which attempt to describe work functions or ion-neutral desorption energies as a function of surface coverage. The first section of Part I deals with theories of atom and ion desorption energies, the second with work function calculations and the third with calculations of potential energies anywhere in front of either a complete array of discrete ions or along a line perpendicular to a single vacancy in such an array. The complete array results are useful for calculations of work function, especially in the high field situation which occurs in field emission. In this case, the applied field cuts the potential barrier to electron emission from the metal so close to the metal that the barrier is diminished by an amount which is related to the coverage of adsorbate and to the value of the applied field. The incomplete array results on the other hand enable ion desorption energies to be computed as a function of coverage.

Not all theories have been reviewed in this work, although it is felt that this review covers most of the main theories of chemisorption, especially those making quantitative predictions of desorption energy and work function.

ATOM AND ION DESORPTION ENERGIES

1 - THE WAVE MECHANICS OF THE SURFACE BOND IN CHEMISORPTION

Advances in Catalysis, 12, 1 (1960)

By T. B. Grimley

Review. - Grimley has elucidated certain qualitative features of chemical adsorption by performing simplified wave-mechanical calculations on one-dimensional chains of atoms, in which each of the m atoms is associated with a single orbital $\psi(r, m)$.

The first part of the calculations was concerned with the properties of a free surface, which in a one-dimensional model is represented by the end atom in a finite chain containing N atoms. Only if the coulomb integral \mathcal{L}_e of the end atom differs significantly from that of other atoms \mathcal{L}_c in the chain will any new electronic properties be introduced. In this case if $|Z| > 1$, where Z is given by $(\mathcal{L}_c - \mathcal{L}_e) / \mathcal{L}_{cc}$, a single localized state of energy, outside the normal band of levels associated with the one-dimensional crystal, will result. The symbol \mathcal{L}_{cc} represents the resonance integral between nearest neighbors in the chain. A state η corresponding to $Z > 1$ will lie above the band in energy, while that corresponding to $Z < -1$, a ρ state will lie below. As $Z \rightarrow \infty$ both of these states will revert to that of a single orbital $\psi(r, m)$.

If, in the three-dimensional model of a finite crystal, containing N^3 atoms, Z is large, the single end state of the linear model becomes a band of states, $8\mathcal{L}_{cc}$ wide, containing N^2 levels; the main crystal band being depleted by the same amount.

Addition of a foreign atom of Coulomb integral \mathcal{L}_f to the finite linear chain may result in separation from the main band of a new localized state. Defining Z , Z_r and η as follows:

$$Z = \frac{\mathcal{L}_c - \mathcal{L}_e}{\mathcal{L}_{cc}}, \quad Z_r = \frac{\mathcal{L}_e - \mathcal{L}_f}{\mathcal{L}_{cc}}, \quad \eta = \frac{\mathcal{L}_{cf}}{\mathcal{L}_{cc}}$$

where \mathcal{I}_{cf} is the resonance integral between the end atom of the chain and the foreign atom, then two localized states may exist in certain regions of the ZZ_r - plane obtained from the two hyperbolas

$$\begin{aligned}(Z + 1) (Z_r + 2) &= \eta^2 \\ (Z - 1) (Z_r - 2) &= \eta^2\end{aligned}$$

In some regions two localized states may exist; these may be two ρ , two η or one each of ρ and η states. In other regions one state only may exist and this can be either ρ or η ; finally, if $\eta^2 < 2$ a forbidden region occurs in which only nonlocalized states exist. Extension of the perturbing influence of the foreign chemisorbed atom to substrate atoms beyond the terminal one leads to the introduction of additional localized states.

Consideration of a three-dimensional model in which perturbation of the crystal by the foreign atom extends only over a group Ω of crystal atoms indicates that a set of localized states associated with the foreign atom and the group Ω may be formed which have energies outside the normal crystal and surface bands. The three-dimensional analogue of the one-dimensional chain with single chemisorbed atom is a crystal lattice completely covered by adsorbate. If $\eta_r = \mathcal{I}_{cf} / \mathcal{I}_{ff} = 1$ where \mathcal{I}_{ff} is the resonance integral between nearest neighbors in the adsorbed layer, then the discrete localized levels (ρ and η) of the one-dimensional model now appear as bands of surface states and each band may contain N^2 levels. Depending on the values of Z and Z_r these bands may or may not overlap the normal band of crystal states. When $\eta_r \neq 1$, one or both bands ρ and η may be incomplete. Complete surface coverage requires at least a complete band of those states which lie below the main crystal band in energy so that if some of these are missing, less than a complete monolayer will be adsorbed on the crystal surface. It is suggested by Grimley that this may provide the mechanism that will account for the decrease in heats of chemisorption with surface coverage.

By considering a linear chain to which two foreign atoms were attached, Grimley was able to investigate the manner in which chemisorbed

atoms interact with one another in chemisorbed layers. If the localized level formed by interaction of a single atom with a crystal does not lie too far below the normal crystal band, the wave function for the localized level is attenuated only slowly in the crystal so that two chemisorbed atoms can interact at distances where the interaction between isolated atoms would be negligible. For two identical atoms attached to the chain at points equidistant from the end, four wave functions for localized states may arise. These are due to ρ and π states and may be even or odd in the center of symmetry of the chain. Provided that a single foreign atom on the chain gives rise to at least one ρ state, then two atoms give rise to an even state. Two ρ states for the single atom give rise to two even states and their energies fall lower as the distance between the adsorbed atoms decreases; the reverse is true for the odd ρ states. In certain circumstances the odd ρ state is missing, its place being taken by an extra level in the nonlocalized crystal band.

Falling heats of chemisorption with coverage can be accounted for in terms of the above concepts: as two atoms adsorbed on the linear chain are brought together the individual localized states belonging to each atom are split into double occupied even and odd states, the latter of which is forced higher and higher in energy until it joins the normal crystal band.

If the foreign atom is chemisorbed by a one-electron bond only, two such chemisorbed atoms should attract each other, because the even ρ state, which is now the only state filled, lies below the state for an isolated chemisorbed atom. Separation of these chemisorbed atoms would raise the energy of the doubly filled even state. This may explain how an activation energy may be involved in the mutual separation of the atoms formed in dissociative chemisorption.

Even though no localized states result when a foreign atom is chemisorbed, binding is still of course possible. The total electronic energy of a chain of identical atoms is:

$$E_n = N \left(\mathcal{E}_c + \frac{4\mathcal{E}_{cc}}{\pi} \right) + \mathcal{E}_{cc} \left[\frac{2}{\pi} (Z + 1/Z) \tan^{-1} Z - (1+Z) \right]$$

It is assumed that there is one electron per atom in the chain, so that the band is half-filled, $\mathcal{J}_{cc} < 0$ and no surface states are occupied. On bringing up a foreign atom to the free end of the chain and assuming for simplicity that $\mathcal{J}_{cf} = \mathcal{J}_{cc}$ and $\mathcal{J}_c = \mathcal{J}_e$ we have a new total system energy:

$$E_{n+1} = (N + 1) \left(\mathcal{J}_c + \frac{4\mathcal{J}_{cc}}{\pi} \right) + \mathcal{J}_{cc} \left[\frac{2}{\pi} (Z_r + 1/Z_r) \tan^{-1} Z_r - (1 + Z_r) \right]$$

The change in total electronic energy when the foreign atom is chemisorbed is given by $\Delta E = E_{n+1} - E_n - \epsilon$ where ϵ is the energy of the valence level electron of the isolated foreign atom.

$$\Delta E = \left[\mathcal{J}_c + \left(\frac{4\mathcal{J}_{cc}}{\pi} \right) - \epsilon \right] + \Delta E_s$$

ΔE_s is the difference in the surface terms in the above equations. The first term is the energy associated with the delocalization of the valence electron on the foreign atom while the second is the change in surface energy caused by the presence of the foreign atom. The delocalization energy is positive or negative according as ϵ lies below or above the mean energy of electrons in the normal band, while ΔE_s is positive according to whether Z_r is greater or smaller than Z . Because of this the two terms tend to cancel. No further information can be gained unless Z or Z_r can be calculated.

Critique. - The ultimate aim of theoretical work dealing with adsorbate-adsorbent interactions is to predict heats of adsorption and work function changes as a function of surface coverage from known physical properties of the solid adsorbate. Grimley's paper contains an outline of an approach which may eventually meet these objectives. It accounts for some of the main features of chemisorption: heats of adsorption which fall as adsorption proceeds, the fact that for some systems saturation occurs when only a fraction of the surface is covered by adsorbate; and it also predicts that an activation energy should be required to separate atoms formed in dissociative chemisorption. However, no quantitative estimates of heats are available so that no quantitative experimental check can be made.

2 - A THEORY FOR ADSORPTION ON METALS

Annales de la Société Scientifique de Bruxelles, T. 80, 140 (1966)

By X De Hemptinne

Review. - A general theory for adsorption on metals has been developed which utilizes a second order perturbation approach involving configuration interaction with an infinite number of interacting configurations. Binding energy is separated into a covalent, ionic and an electrostatic contribution, this last quantity being merely the result of the attraction of an ion with its image in the metal.

As the molecule approaches the metal, the change in geometry of the system gives rise to interactions which may be represented both by diagonal and by nondiagonal matrix elements. The first order energy correction is equal to the diagonal matrix element of the perturbation with the configuration which describes the nonperturbed situation, i. e., $\langle a | \mathcal{V}_p | a \rangle$. Nondiagonal matrix elements, $\langle \beta | \mathcal{V}_p | a \rangle$, couple different configurations, which appear only in second and higher order terms. If $|a\rangle$ is a system wave function whose configuration represents the system without interaction between its parts (energy: $E_0 = \langle a | H | a \rangle$) and $|\beta_i\rangle$ is a wave function whose configuration is derived out of $|a\rangle$ by electron transitions (energy: $E_i = \langle \beta_i | H | \beta_i \rangle$), then the energy of the system during interaction is a root of the secular equations.

$$\Delta E \prod (\Delta E + w_i) - \sum \langle \beta_i | H | a \rangle^2 \prod (\Delta E + w_i) = 0 \quad (1)$$

where $w_i = E_i - E_0$, \prod represents a product in which all indices are represented except i and $\Delta E = E_0 - E$ where ΔE is the change in energy of the system due to adsorption. This equation is solved by replacing ΔE by the complex variable $x + yj$, dividing by $\prod (x + jy + w_i)$ and taking the limit $y \rightarrow 0$. After taking the real part of the resulting expression we have

$$x - \sum_{y \rightarrow 0} \frac{K_{\beta_i} |H| a|^2}{(x+w_i)^2 + y^2} (x + w_i) = 0 \quad (2)$$

It has been shown¹ that the sum of the squares of the matrix elements which couple the ground state $|a\rangle$ to all possible configurations with the same energy E_i is equal to the product of the density $[G(E_i)]$ of configurations with energy E_i and a term V_p^2 which is a measure of the intensity of coupling

$$\sum \langle \beta_i | H | a \rangle^2 = \langle V_p^2 \rangle G(E_i) dE \quad (3)$$

with energy E_i .

After further manipulation in which the above sum was replaced by integration, $G(E_i)$ was replaced by $G(w+x)$ and expressed in terms of $G'(w)$, $G''(w)$ etc., the following first approximation to ΔE was obtained,

$$\Delta E = \langle V_p \rangle^2 \int dw G(w) P(1/w). \quad (4)$$

To second approximation,

$$\Delta E = \frac{\langle V_p \rangle^2 \int dw G(w) P(1/w)}{1 - \langle V_p \rangle^2 \int dw G'(w) P(1/w)} \quad (5)$$

where $P(1/w) = \lim_{y \rightarrow 0} w/(w^2 + y^2)$.

The covalent contribution to bonding energy, which may be calculated by considering the energy of the configuration that results from an exchange of an electron between the metal and adsorbate, depends on the split in energy between the bonding and antibonding orbitals in the adsorbed molecule. If the molecule chosen is ethylene, then the orbitals concerned are the π bonding and antibonding orbitals with the two lowest excitation energies are given by

$$\text{Singlet} \longrightarrow \text{Triplet} = 0.81 - (\mathcal{J}_{cc} + \mathcal{J}_{cc}^*) \quad (\text{eV}) \quad (6)$$

$$\text{Singlet} \longrightarrow \text{Singlet} = 1.95 - (\mathcal{J}_{cc} + \mathcal{J}_{cc}^*) \quad (\text{eV}) \quad (7)$$

where \mathcal{J}_{cc} is the resonance integral for the bonding orbital and \mathcal{J}_{cc}^* is the

corresponding value for the antibonding orbital. The quantity ΔE for singlet-to-triplet transitions in the adsorption situation is then given by

$$\Delta E_{\text{cov}} = \langle V_P \rangle^2 \int dE_1 \int dE_2 \frac{g(E_1) g(E_2) \exp(E_2 - E_F)/kT}{[1 + \exp(E_1 - E_F)/kT][1 + \exp(E_2 - E_F)/kT]} \times \frac{1}{P} \frac{1}{E_1 - E_2 + 0.81 - (q_{cc} + q_{cc}^*)} \quad (8)$$

where $E_1 - E_2 + 0.81 - (q_{cc} + q_{cc}^*)$ represents the energy change due to a covalent electron transition in which an electron from a filled state of the metal, E_1 , has made a transition to the excited triplet state of ethylene while the other has made the transition from the ground state of ethylene to an empty metal level E_2 . The term $g(E_1)/[1 + \exp(E_1 - E_F)/kT]$ is the occupation number of the level E_1 , and the number of vacant levels with energy E_2 is $[dE_2 g(E_2) \exp(E_2 - E_F)/kT] / [1 + \exp(E_2 - E_F)/kT]$. An equation similar to equation 8 for singlet-to-singlet transitions for the adsorption energy of ionic bonds are as follows:

$$\Delta E_r = \int dE_1 \frac{g(E_1)}{1 + \exp(E_1 - E_F)/kT} P \left(\frac{1}{E_1 - E_\pi^*} \right) \langle V_r \rangle^2 \quad (9)$$

$$\Delta E_o = \int \frac{dE_2 g(E_2) \exp(E_2 - E_F)/kT}{1 + \exp(E_2 - E_F)/kT} P \left(\frac{1}{E_\pi - E_2} \right) \langle V_o \rangle^2 \quad (10)$$

in which ΔE_r is the energy of the bond arising from an electron transfer into the metal, while ΔE_o is that derived from electron transfer in the opposite direction. Note that E_F is the energy of the Fermi level. The matrix elements may be taken out of the integration signs and the integrals which remain are functions of $(E_\pi - E_F)$ and $(E_\pi^* - E_F)$. These quantities may be expressed as:

$$E_F - E_\pi = (5.4 + q_{cc}) - \phi - e^2/2r \quad (\text{eV}) \quad (11)$$

$$E_\pi^* - E_F = (0.46 - q_{cc}^*) + \phi - e^2/2r \quad (\text{eV}) \quad (12)$$

where $(5.4 + I_{cc})$ is the ionization energy of ethylene, $(0.46 - A_{cc})$ is the electron affinity of ethylene, ϕ is the work function of the metal and $e^2/2r$ is the coulomb interaction between metal and ion. Now the following empirical relation holds: $(I_{cc} + I_{cc}^*) = 45 \exp(-1.17 r_{c-c}^2)$ where r_{c-c} is the c-c bond distance in Å, so that the c-c bond energy is greater for smaller values of r_{c-c} ; on the other hand, binding of the molecule to the surface is favored by larger values of r_{c-c} . A compromise is reached between the adsorption and the c-c dissociation energy so that total energy is at a minimum. The value of r_{c-c} at the minimum is obtained by differentiating the total energy expression and equating to zero:

$$\frac{\partial}{\partial r} \left[E_2 + \frac{61.17}{2} (r - 1.33)^2 + \Delta E_o + \Delta E_r + \Delta E_{cov} \right] = 0 \quad (13)$$

where E_2 is the ground state energy of ethylene and 61.17 is the force constant of ethylene expressed in eV/Å². The binding energy of ethylene on the metal is then obtained from Equation (13) by reinserting the value of r at the minimum binding energy. In order to derive a numerical estimate of binding energy, the value of $\langle \psi_p^2 \rangle$ is needed for the various configurations. Unfortunately it is not possible to make an accurate calculation of $\langle \psi_p^2 \rangle$ so that no numerical assessment of the binding energy is possible at this time.

Critique. - Hemptinne has developed a general theory of chemisorption which distinguishes between covalent adsorption and two types of ionic adsorption: that in which an electron is transferred from adsorbate atom to the metal and that in which electron transfer is in the other direction. No method for dealing with interactions between neighboring adsorbed particles was included so that the theory does not predict how heats of adsorption depend on surface coverage. Because the final expression for adsorption energy contained a term $\langle \psi_p^2 \rangle$, determined by the intensity of coupling between different configurations, which was not readily calculable, no check with experiment was possible.

¹X de Hemptinne, Bull. Soc. Chim. France, 1964, 2320.

3 - THE THEORY OF CHEMISORPTION

Kinetics and Catalysis 3, 612 (1962)

by V. D. Sutula

Review. - This paper contains a one-dimensional quantum mechanical treatment of adsorption in which the author has discussed formation of an adsorbate atom on the end of a linear chain of substrate atoms. The surface state lies above the main substrate band and is an antibonding level. By drawing analogy with the example of bond formation in diatomic molecules, the author has stated that treatment of gas-solid interactions can be limited to the interaction of the gas molecule with a single surface atom of the solid formally replacing the orbital of the atom, $\psi(x)$ by $\lambda\psi(x)$. In this way the author reduces the problem to the solution of the secular equation:

$$\begin{vmatrix} E - E_{oA} - J_f & J_{cf} & 0 \\ J_{cf} & E - E_o - J_e & \lambda J_{cc} \\ 0 & \lambda J_{cc} & E - E_o - J_c \end{vmatrix}$$

which must be solved to first order in λ^2 ; λ^2 then being set equal to unity. In the secular determinant above E_{oA} is the energy level of the adsorbate atom in the free state, while E_o is the energy level of the lattice atom in the free state. It is assumed that E_{oA} is higher than E_o . The quantities J_c , J_e , and J_f are the Coulomb integrals for the atoms in the chain, the end atom and the foreign adsorbed atom respectively. The exchange integral for the orbitals of atoms in the chain is J_{cc} , that for the orbital of the end atom and the foreign atom is J_{cf} . Two of the solutions for E are:

$$E_{ads} = \frac{E_A + E_1}{2} + \sqrt{v^2 + J_{cf}^2} + \frac{J_{cc}^2}{2} \frac{\sqrt{v^2 + J_{cf}^2} + v}{\sqrt{v^2 + J_{cf}^2} (\sqrt{v^2 + J_{cf}^2} - u)} \quad (1)$$

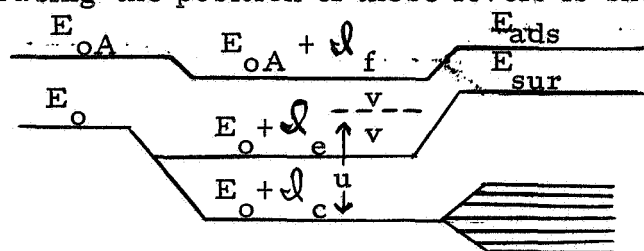
$$E_{\text{sur}} = \frac{E_A + E_1}{2} - \sqrt{v^2 + \mathcal{L}_{\text{cf}}^2} + \frac{\mathcal{L}_{\text{cc}}^2}{2} \frac{v - \sqrt{v^2 + \mathcal{L}_{\text{cf}}^2}}{\sqrt{v^2 + \mathcal{L}_{\text{cf}}^2} (\sqrt{v^2 + \mathcal{L}_{\text{cf}}^2} + u)} \quad (2)$$

where E_{ads} is the energy level formed from the level of the adsorbate and E_{sur} is the surface level in the solid body. Also,

$$v = \frac{E_n - E_a}{2} ; \quad u = E_1 - \frac{E_n + E_a}{2}$$

$$E_n = E_o + \mathcal{L}_e, \quad E_1 = E_o + \mathcal{L}_c, \quad E_a = E_{oA} + \mathcal{L}_f$$

A diagram illustrating the position of these levels is shown below



The first two members of equations (1) and (2) arise from the interaction of the adsorbed atoms and the surface atom while the last term is a result of interaction with the rest of the solid; it makes a positive contribution to E_{ads} since $u < 0$ and $v < 0$. Adsorption is accompanied by an increase in energy with a corresponding rise in the level E_{ads} if the bond and the surface level are both filled while the level of the adsorbed atom is vacant. This effect becomes more pronounced as the surface level approaches the level of the atom which is undergoing adsorption and v diminishes. A similar situation occurs when the level of the adsorbed atom is filled and lies beneath an empty bond.

Critique. - Like Grimley's one-dimensional treatment,¹ this paper offers no quantitative estimate of adsorption heats so that no experimental check can be made. The analogy between adsorption bonding and bonding in diatomic molecules, drawn in this paper was also made by Gyftopoulos and Levine.² Whereas the latter authors used a phenomenological approach which enabled them to calculate heats of adsorption in terms of the properties

of the adsorbate and substrate, Sutula has used more sophisticated LCAO wave mechanical approach which has provided much insight into diatomic molecular bonding.

¹R. W. Grimley, Advances in Catalysis 12, 1 (1960).

²J. D. Levine and E. P. Gyftopoulos, Surface Science 1, 171 (1964).

4 - THE THEORY OF CHEMICAL ADSORPTION

Doklady, Akad, Nauk, (USSR), 130, 9 (1960)

By V. I. Asherov

Review. - Asherov has formulated a quantum mechanical treatment of surface adsorption in which the single electron Hamiltonian for a system of particles interacting with a crystal is expressed as

$$H = \frac{-\hbar^2}{2m} \nabla^2 + V_1 + V_2$$

where V_1 is the potential energy for the undisturbed crystal and V_2 is the potential energy of the adsorbed particles if no account is taken of interaction with the crystal. The eigenfunction ψ_I corresponding to this Hamiltonian was expressed as a linear combination of the eigenfunctions of the crystal, ψ_k and of the system of particles $\sum c_n \psi_n$

$$\psi_I = S + a_k \psi_k + \sum a_n \psi_n \quad (1)$$

where k denotes both the zone number and the wave vector within it, n is the location of the adsorbed particle. S denotes summation over the zone numbers and integration with respect to the momentum among them. The coefficient a_k and a_n were determined from the requirement that the eigenvalue, E , of Equation (1) should be a minimum. For the case of adsorption of one particle, the problem devolves into finding the roots of

$$1 - S \langle \psi_n | V_k | \psi_k \rangle \langle \psi_k | V_k^{-1} | \psi_n \rangle = 0$$

where

$$V_k = \frac{E_k - E + V_2}{E_0 - E + V_1}$$

and E_k is the eigenvalue corresponding to ψ_k and E_0 is the eigenvalue corresponding to $\sum c_n \psi_n$

When many particles are adsorbed, account must be taken of nearest neighbors to the adsorbed particle n . If the nonorthogonality of ψ_k and ψ_n is neglected and it is assumed that there is substantial localization of the adsorbate bond, then E is given by

$$E = E_{k,o} + \frac{4\pi n\theta \langle \psi_n V_2 \psi_k \rangle \langle \psi_k V_1 \psi_n \rangle}{(E_k - E_o)} \quad (2)$$

where n is the number of nearest neighbors, θ is the degree of surface coverage and $E_{k,o}$ is independent of θ . The differential heat of adsorption is found from

$$q_d(\theta) = S (E_k - E) + E_o \quad (3)$$

where S is taken with respect to occupied positions. We now have from equations (2) and (3)

$$q_d(\theta) = q_d(0) - \frac{u n \langle \psi_n V_2 V_1 \psi_n \rangle}{|E_{ko} - E_o|} \quad (4)$$

where $q_d(0)$ is the initial heat of adsorption, E_{ko} is the mean energy of the electrons in the valence band of the crystal and u is the ratio of the volumes bounded by the Fermi surface, and the surface of the nearest Brillouin zone. The last term in Equation (4) is approximately 1 eV for $\Delta\theta = 1$.

Critique. - Although the theory presented by this author is brief, it is the only *a priori* treatment of adsorption discussed in these reviews which provides information on the variation of heats of adsorption with surface coverage. The theory is applicable to adsorption on dielectrics as well as on metals. A total decrease of ~ 1 eV was estimated for the change in heat of adsorption due to adsorption of a monolayer of adsorbate. This agrees fairly well with experimental values. The fact that equation (2) was derived on the assumption of substantial localization of the adsorbate bond means that it is probably not applicable to nonlocalized bonding, e.g., metallic adsorption.

5 - APPLICATION OF THE CHARGE-TRANSFER NO-BOND THEORY TO ADSORPTION PROBLEMS

Trans. Faraday Soc. 56, 846 (1960)

By P. M. Gundry and F. C. Tompkins

Review. - Gundry and Tompkins discuss in this paper the charge-transfer no-bond resonance theory, developed by Weiss,¹ Brackmann² and Mulliken³ and applied by Tuck⁴ and incorrectly by Brodd⁵ to the problem of adsorption. Let the wave function of the adsorption complex be Ψ_{Mg} , then

$$\Psi_{Mg} = a\Psi_{NB} + b\Psi_D$$

where Ψ_{NB} , Ψ_D are the wave functions of the no-bond and dative states and a, b are constants chosen to maximize Ψ_{Mg} . Normalization results in

$$\Psi_{Mg} = (\Psi_{NB} + \lambda \Psi_D) / (1 + \lambda^2 + 2\lambda S)$$

where $\lambda = b/a$ and $S = \int \Psi_{NB} \Psi_D d\tau$. On solving the secular equations, with the resonance integral, $\int \Psi_{NB} H \Psi_D d\tau$ represented by \mathcal{J}_{cf}

$$-W_{Mg} = \left[\frac{2\mathcal{J}_{cf}S + W_{NB} + W_D \pm \left\{ (2\mathcal{J}_{cf}S - W_{NB} - W_D)^2 - 4W_{NB}W_D + 4\mathcal{J}_{cf}^2 \right\}^{1/2}}{2(1 - S^2)} \right]$$

For $S = 0$ Equation (1) reduces to

$$-W_{Mg} = 1/2 \left[(W_{NB} + W_D) \pm \left\{ (W_D - W_{NB})^2 + 4\mathcal{J}_{cf}^2 \right\}^{1/2} \right]$$

The heat of formation of the surface complex at zero coverage is then

$$E_S = (W_M + W_g - W_{Mg}) = (W_M + W_g - W_{NB}) + (W_{NB} - W_{Mg})$$

where W_{Mg} is the resonance energy and W_M , W_g the energy of the metal and adsorbate referred to a standard state. The term $W_D - W_{NB}$ is given by

$$W_D - W_{NB} = \phi - E_A - e^2/4r \quad (2)$$

where the metal is acting as an electron donor. In this expression, ϕ is the work function of the metal, E_A is the electron affinity of the adsorbate. The quantity $2r$ is the distance between the center of charge and its image. When the adsorbate acts as donor, we have

$$W_D - W_{NB} = V_I - \phi - e^2/4r \quad (2)$$

where V_I is the ionization potential of the adsorbate. It is assumed that $W_M + W_g = W_{NB}$ so

$$2E_S = -(W_D - W_{NB}) \pm \left\{ (W_D - W_{NB})^2 + 4\phi_{cf}^2 \right\}^{1/2}$$

Brodd⁵ equated ϕ_{cf} to $\Delta\phi$ the work function change on adsorption, but Gundry and Tompkins demonstrated that the calculated values of E_o are unacceptable and conclude that the method is inapplicable to chemisorption problems; in this case the correct quantum mechanical formulation is that of Higuchi, Ree and Eyring.⁶

The method is, however, applicable to physical adsorption; although in this case, it is necessary to take into account the dispersion energy E_d which also contributes to the heat of adsorption $E = E_o + E_d$. A relation $\Delta\phi$ and E_o may be established as follows: E_o is a root of Equation (1), given approximately by

$$E_S = \frac{(\phi_{cf} - S W_{NB})^2}{W_D W_{NB}} \quad (3)$$

The dipole moment μ of the adsorption bond given by Gundry and Tompkins is

$$M \approx e r \left[\frac{(\lambda^2 + 2\lambda S)}{1 + \lambda^2 + 4\lambda S / (2 + 2S^2)^{1/2}} \right]$$

A similar expression is given by Coulson.⁷

The quantity λ , which is a measure of the surface bond polarity, may be derived from second order perturbation theory and is given by

$$\lambda \approx \frac{(Q_{cf} - S W_{NB})}{W_D - W_{NB}} \quad (4)$$

From the Equations (3) and (4) we obtain

$$\lambda^2 \approx E_S / (W_D - W_{NB})$$

For small values of λ and S ,

$$M \approx e r \lambda^2 = e r E_S / (W_D - W_{NB}) \quad (5)$$

and $\Delta\phi$ may be obtained from the Helmholtz equation

$$\Delta\phi = 4\pi\sigma_o \theta M \quad (6)$$

where σ_o is the number of adatoms per unit area and θ is the relative surface coverage. Hence M may be obtained from Equation (5) with $W_D - W_{NB}$ given by Equation (2).

In another approach, Gundry and Tompkins considered $E_S = \alpha F^2/2$ where α is the polarizability of the adsorbate. From this $\Delta\phi$ was evaluated by using $M = \alpha F$ in Equation (6). Since both this approach and that of the no-bond resonance theory gave results which were in accord with experiment, the authors were undecided about which theory was the more applicable.

Critique. - This paper of Gundry and Tompkins is a valuable short review of several earlier theories of low coverage heats of adsorption. The authors conclude that the charge transfer theory is not applicable to chemisorption problems at all. It may, however, be applicable to physical adsorption situations, although even here its validity is uncertain.

- ¹ Weiss, J. Chem. Soc. 245, (1942).
- ² Brackmann, Rec. Trav. Chim. 68, 147 (1949)
- ³ Mulliken, J. Am. Chem. Soc. 74, 811 (1952).
- ⁴ Tuck, J. Chem. Phys. 29, 724 (1958).
- ⁵ Brodd, J. Physic. Chem. 62, 54 (1958).
- ⁶ Higuchi, Ree and Eyring, J. Am. Chem. Soc. 79, 1330 (1957).
- ⁷ Coulson, Valence, Oxford, Chapter 9, P. 104 (1952).

6 - ADSORPTION PHYSICS OF METALLIC SURFACES PARTIALLY COVERED BY METALLIC PARTICLES I ATOM AND ION DESORPTION ENERGIES

Surface Sci. 1, 171 (1964)

By J. D. Levine and E. P. Gyftopoulos

Review. - In their paper I of 1964, Gyftopoulos and Levine continued their phenomenological approach which makes use of certain concepts developed in molecular physics. Thus, they draw the analogy between the energy of dissociation of diatomic molecules on the one hand and the energy of desorption or sublimation of adsorbed atoms from solids on the other.

It is assumed that metal-adsorbate bonds may be partly ionic and partly covalent so that desorption energy E_a can be represented by:

$$E_a = H_{ii} + H_{cc} \quad (1)$$

where H_{ii} is the ionic contribution to the bond and H_{cc} is the covalent contribution. E_a was calculated subject to the following conditions:

1. H_{ii} vanishes for a purely covalent bond.
2. H_{cc} vanishes for a purely ionic bond.
3. H_{cc} reduces to heat of sublimation of material from its own lattice when the heat of desorption of material from surface of the same bulk material is considered.

H_{ii} is assumed to arise from a fraction of charge f_q of the adsorbate which is transferred to the substrate. f_q determines the partial ionic character of the bond and is associated with surface dipole moment. By means of a Born Haber type of thermodynamic cycle calculation, the following expression for H_{ii} was derived:

$$H_{ii} = f_q \phi [1 + \delta] \quad (2)$$

where

$$\delta = \frac{f_q}{\phi} \left(\frac{e^2}{R} - V_I \right) \quad (3)$$

and where R is the internuclear distance between substrate and adsorbate. V_I is the ionizing potential of the adsorbate. ϕ has been calculated in a previous paper of Gyftopoulos and Levine and is the work function of the composite surface.

H_{cc} was assumed to be a function of E_f , the heat of sublimation of the adsorbate, L_f the angular strength of the adsorbate valence orbital, q_f the valence charge of the adsorbate and a function of corresponding quantities of the metal. The adsorbate contribution to H_{cc} is assumed to be proportional to $E_f L_f^2 q_f$. Inclusion of E_f ensures that H_{cc} is equal to E_f when the adsorbate is adsorbed on its own bulk material while the L_f^2 concept has been used successfully by Pauling. L_f depends on what valence orbital participates in the bond. Thus, $L_f = \sqrt{1}$ for s-orbitals, $\sqrt{3}$ for p orbitals etc. q_f was included so that H_{cc} vanished when a purely ionic bond is formed, in which case, $q_f = 0$. The simplest expression for H_{cc} which combines the following:

$$\begin{aligned} H_{cc} &\propto E_f L_f^2 q_f && \text{contribution of the adsorbate} \\ H_{cc} &\propto E_m L_m^2 q_f && \text{contribution of the metal substrate} \end{aligned}$$

and guarantees that the limiting requirements $-H_{cc} = E_f$ for $m = f$ and $H_{cc} = 0$ for $q_f = 0$ is the normalized geometric mean.

Both q_f and q_m are related to f_q and to the largest number of valence electrons N_v that can participate in the covalent bond: $q_f = N_v - f_q$ and $q_m = N_v + f_q$. The final expression for the covalent part of the desorption energy is:

$$H_{cc} = (E_f E_m)^{1/2} L_{fm} Q_{fm} \quad (4)$$

where L_{fm} may be interpreted as the angular efficiency of the orbitals, and Q_{fm} as the charge efficiency.

Putting the expression for H_{ii} (Equation (2)) and for H_{cc} (Equation (4)) into Equation (1) yields the desired theoretical expression for the

desorption energy of atoms.

The ion desorption energy E_p can be derived by using a similar Born Haber type of calculation and is shown to be related to the atomic desorption energy E_a and to the work function of the composite surface, ϕ , by:

$$E_p = E_a + V_I - \phi \quad (5)$$

where V_I is the ionization potential.

Critique. - The phenomenological approach used by these authors to calculate atom and ion desorption energies yields values of E_a and E_{ao} which are in good agreement with experiment. Thus, their values of E_a follow closely the experimental values determined by Langmuir and Taylor;¹ moreover, good agreement between theory and experiment was found for a range of E_{ao} values between 2.5 eV and 8.0 eV.

The theoretical expression for the electron work function ϕ which was obtained by Gyftopoulos and Levine has been criticized in an earlier part of this report. However, since the functional dependence of ϕ on θ was severely constrained by the imposed boundary conditions (i. e., $\phi = \phi_f$ when $\theta = 1$ and $\phi = \phi_m$ when $\theta = 0$ etc.) an error in ϕ does not seriously affect the final calculated value of E_a . In the case of E_{ao} , ϕ devolves to ϕ_m , the work function of the clean substrate, so that no error is introduced in the calculation of E_{ao} by an incorrect formulation of ϕ .

In the absence of any detailed quantum mechanical models of adsorption which yield predicted values of E_a , the model of Gyftopoulos and Levine fulfills an important need.

¹ I. Langmuir and J. B. Taylor, Phys. Rev., 44, 423 (1933).

7 - ADSORPTION KINETICS I
THE SYSTEM OF ALKALI ATOMS ON TUNGSTEN

J. Am. Chem. Soc. 77, 4969, (1955)

By I. Higuchi, T. Ree and H. Eyring

Dependence of $\Delta\phi$ on θ . - The authors have derived an expression for the variation of ϕ versus θ based on the Helmholtz equation:
 $\Delta\phi = 4\pi\sigma_o \theta \text{ er}/\epsilon$, where σ_o is the adsorption site density, r is the distance between the ion and the metal surface and ϵ is the dielectric constant of the adsorbed layer. By using classical electrostatic concepts and assuming that the adsorbed layer could be approximated as a structureless dielectric, ϵ was expressed as $\epsilon = 1 + c \alpha \theta$ where $c = 4\pi\sigma_o/r$ and α is the polarizability of the adsorbed layer. Consequently $\Delta\phi = V_o \theta / (1 + c\alpha\theta)$, where $V_o = 4\pi\sigma_o M$.

Dependence of ΔH on θ . - The zero coverage heat of adsorption ΔH_o was assumed to be given by de Boer's equation¹: $\Delta H_o = e\phi - V_I + e^2/4r$, while the variation of ΔH with coverage of a layer of ions was calculated as follows: the adsorbed layer was thought of as behaving electrically like a parallel plate condenser so that the electrostatic energy of the adsorbed layer is given by $\bar{E}_f = D^2 r / 8\pi\epsilon$, due to the adsorption of $\sigma_o \theta$ ions. The field energy, E_f , created by one ion adsorbed is given by

$$E_f = \frac{\partial \bar{U}_f}{\partial (\sigma_o \theta)} = \frac{r}{8\pi\sigma_o} \left(2D \frac{\partial D}{\partial \theta} - \frac{D^2}{\epsilon^2} \frac{\partial \epsilon}{\partial \theta} \right)$$

which on substituting $D = \epsilon F$, $F = \Delta\phi/r$ and $\epsilon = 1 + c \alpha \theta$ yields

$$E_f = \frac{cM^2\theta}{1 + c\alpha\theta} - \frac{c^2 M^2 \theta^2 \alpha}{2(1 + c\alpha\theta)^2} \quad (1)$$

In addition to the image force, the ion is subjected to other attractive forces when it is adsorbed on a partly covered surface. These arise from the interaction between the ion and the image charges of its neighboring adsorbed ions. If the image charges are assumed to be smeared out in a plane parallel to the surface, then the potential energy of the ion due to the charge

on an element of surface area ds is

$$dE_i = - \frac{\sqrt{\epsilon_0} q e^2 ds \cos(\theta)}{(1 + \alpha \epsilon_0 \theta) r} \quad (2)$$

where r is the distance between the ion and the charge element ds and θ is the angle between the line perpendicular to the surface through the ion and the line, r , joining the ion and the surface element ds . Use has been made of the relation $\epsilon(\theta) = \epsilon / \cos(\theta)$ where $\epsilon(\theta)$ is the effective value of ϵ along r . The quantity $\sqrt{\epsilon_0}$ is an empirical factor $0 < \sqrt{\epsilon_0} < 1$ to take into account repulsive interactions between the representation and neighboring positive ions. To obtain fit with experiment $\sqrt{\epsilon_0}$ was set equal to $1/4$. Assuming that the image charges are uniformly distributed in the surface, then if the surface element is in the form of a ring centered about the ion, $ds = 2\pi r^2 \tan(\theta) d\theta$. Integration yields

$$E_i = \frac{cM^2 \theta A}{4(1 + \alpha \epsilon_0 \theta)} \quad (3)$$

where $A = \ln(\cos(\theta_c))$. The quantity θ_c is the upper limit of the integration, zero being the lower limit. The upper limit θ_c is the angle at which shielding by neighbors of the image forces is complete and $\cos(\theta_c)$ is given by $\cos(\theta_c) = r_i/d$ where r_i is the radius of the ion and d is related to θ by $d = d_1/\sqrt{\theta}$. Note that d_1 is the distance between two adsorbed ions when $\theta = 1$, hence

$$E_i = \frac{-cM^2 \theta \ln(d_1/r_i \sqrt{\theta})}{4(1 + \alpha \epsilon_0 \theta)}$$

Now $S(\Delta H) = E_f + E_i$, so that

$$S(\Delta H) = \frac{cM^2 \theta}{1 + \alpha \epsilon_0 \theta} \left\{ 1 - \frac{\alpha \epsilon_0 \theta}{2(1 + \alpha \epsilon_0 \theta)} - \frac{1}{4} \ln(d_1/r_i \sqrt{\theta}) \right\} \quad (4)$$

This equation gives the coverage dependent part of the heat of ionic adsorption, and the total heat of adsorption $\Delta H = \Delta H_0 + S(\Delta H)$.

Critique. - The work function expression derived by these authors is a simple modification of the Helmholtz equation which is reduced by a dielectric factor related to the polarizability of the adsorbed ions. As such the model is a simple classical electrostatic one and as with other models agreement is good in the region of low coverage ($\theta < 0.5$) only. At higher surface coverage of adsorbate, the model does not predict the minimum which is observed in the alkali metal/alkaline earth systems. This is not surprising since it appears that the minimum is a function of the closest adsorbate packing arrangement which registers with the underlying substrate and no cognizance of such effects is contained in this model.

In view of the inclusion of the adjustable factor $\sqrt{\epsilon}$ in Equation (2), Equation (4) for the variation of ΔH with coverage θ is a semiempirical expression derived solely from classical electrostatic considerations. It is surprising then to note the good agreement between theory and Langmuir's experimental data for the cesium/tungsten system. Less good agreement was obtained for the system sodium/tungsten, although in this case the experimental data points were somewhat erratic.

¹ J. H. de Boer, *Electron Emission and Adsorption Phenomena*, The MacMillan Co., New York 1935, p. 81.

8 - ADSORPTION KINETICS II NATURE OF THE ADSORPTION BOND

J. Am. Chem. Soc. 79, 1330 (1957)

By I. Higuchi, T. Ree and H. Eyring

Review. - In this paper the authors derive expressions for heats of desorption as a function of coverage for ionic and covalent adsorption.

If the surface atoms of an adsorbent have unpaired electrons, these may interact with the electrons of an adsorbate to form polar bonds analogous to those formed in molecules. The fraction, C_i^2 , of ionic character in the bond is given by

$$\frac{1}{C_i^2} = 1 + \frac{E_s - H_{ii}}{E_s - H_{cc}} \quad (1)$$

where E_s is the energy of the adsorption bond, H_{ii} and H_{cc} are the energies for ideal ionic and covalent bonds, respectively. To a first order approximation, H_{ii} and H_{cc} are given by

$$H_{ii} = E_A - V_I + \frac{8e^2}{9R} \quad (2)$$

and

$$H_{cc} = \left\{ E(M - M) + E(A - A) \right\} / 2 \quad (3)$$

where R is the distance between atoms M and A , E_A is the electron affinity of the electron acceptor and V_I , the ionization potential of the donor. The quantities $E(M - M)$ and $E(A - A)$ are the bond energies of the single bonds $M - M$ and $A - A$ respectively. The bond moment is expressed as $\mu = C_i^2 e R$, so that C_i^2 may be obtained from the Helmholtz equation $\Delta\phi = 4\pi\theta \sigma_o \mu / \epsilon$ where σ_o is the density of adsorption sites, μ is the dipole moment and ϵ is the dielectric constant of the adsorbate layer. Hence E_s may be obtained from Equation (1) using the value C_i^2 and values for H_{ii} and H_{cc} derived from Equations (2) and (4) respectively.

An alternative method of calculating E_s is from the following approximate relation pointed out by Pauling¹:

$$E_s = H_{ii} + (X_M - X_A)^2$$

where X_M and X_A are the electronegativities of M and A respectively. When $X_M - X_A$ is small, the further approximation also applies:

$$E_s = H_{ii} + \mu^2$$

Zero coverage activation heats of desorption are related to E_s via

$$\Delta H_o = E_s \quad (5)$$

for desorption of monatomic gases and

$$\Delta H_o = 2E_s - E(A - A) \quad (6)$$

for diatomic gases which adsorb dissociatively. As discussed in paper 7, ΔH_o for ionic adsorption is given by

$$\Delta H_o = e\phi - V_I + \frac{e^2}{4r} \quad (7)$$

where r is the distance of the adion from the surface. For pure covalent adsorption $E_s = H_{cc}$ since $C_i^2 \simeq 0$. Hence from Equation (6) above, $\Delta H_o = E(M - M)$ for the dissociative adsorption of homonuclear gases on metals. In general, adsorption bonds are partially ionic and in order to calculate the bond energy, Equation (1) must be used, C_i^2 being obtained from work function measurements and the Equation $\mu = C_i^2 eR$ mentioned above. The quantity ΔH_o is then obtained from Equation (5) and (6).

Calculation of H_{cc} in Equation (3) requires knowledge of $E(M - M)$. This latter quantity may be obtained from the vaporization heat of the metal λ by means of the equation: $E(M - M) = \chi \lambda$ where $\chi = 2/12$ for f. c. c. metals in which each atom has 12 nearest neighbors and $2/8$ for b. c. c. metals in which each atom has 8 nearest neighbors. For multiple bonds

E is calculated from Equation (1) with H_{cc} and H_{ii} for $\mu = 0$ given by

$$H_{cc} = \left\{ 2E (M - M) + D(O_2) \right\} / 2$$

$$H_{ii} = 1/2 \left\{ 2E (M - M) + D(O_2) \right\} / 2 + A_O - V_I + (8/9) (e^2/R)$$

$$H_{cc} = \left\{ 3E (M - M) + D(N_2) \right\} / 2$$

$$H_{ii} = 2/3 \left\{ 3E (M - M) + D(N_2) \right\} + E_A - V_I + (8/9) (e^2/R)$$

The variation of activation heats of desorption with coverage may be estimated from Equation (3) of paper 7 of this series.² Equation (4) was derived for ionic desorption and is given by

$$S(\Delta H) = \frac{c\mu^2\theta}{1 + c a \theta} \left\{ 1 - \frac{c a \theta}{2(1 + c a \theta)} \right\} - \frac{c\mu^2\theta}{4(1 + c a \theta)} \left\{ \ln \frac{d_i}{r_i \sqrt{\theta}} \right\}$$

If $c a \theta \ll 1$ and E_i (defined in paper 7) is very small

$$S(\Delta H) = c\mu^2\theta = 2\pi\sigma_O e \mu \theta = e \Delta \phi$$

For dissociative adsorption of homonuclear diatomic molecules

$$S(\Delta H) = 2 e \Delta \phi$$

so that measurement of $\Delta \phi$ as a function of θ enables $S(\Delta H)$ to be determined conveniently.

Critique. - This fairly simple formulation for the zero coverage heat of desorption and for the variation of heat of desorption for covalent and ionic adsorption describes reasonably well the experimental data for a variety of systems. The description of covalent systems holds only if $c a \theta \ll 1$, and if E_i is very small. For many systems, however, this will not be true. A major weakness for adsorption of electronegative gases is that no account is taken of the existence of multiple binding states on individual planes.

Eley³ estimated the bond energy of metal-hydrogen bonds by assuming them to be predominantly covalent and adopting Pauling's rule¹ for the strength of such bonds in diatomic molecules. According to Gundry and Tompkins, the above approach of Higuchi, Ree and Eyring amounts to a reformulation of Eley's approach in quantum-mechanical terms.

¹ L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 60.

² I. Higuchi, T. Ree and H. Eyring, J. Am. Chem. Soc. 77, 4969 (1955).

³ Eley, Faraday. Soc. Disc. 8, 34 (1950).

9 - PENETRATION OF AN ION THROUGH A MONOLAYER OF SIMILAR IONS ADSORBED ON A METAL

J. Appl. Phys. 36, 357 (1965)

By J. W. Gadzuk and E. N. Carabateas

Review. - In their paper of 1965, Gadzuk and Carabateas derived ion penetration coefficients for the limiting cases of mobile and immobile adsorption of ions on a metal substrate and also for the case of a partially mobile adsorbate film. The penetration coefficient f is defined as follows:

$$f = \frac{\Delta\phi_i}{\Delta\phi} \quad (1)$$

where $\Delta\phi$ is the change in electron work function at any coverage θ , and $\Delta\phi_i$ is the change in ionic work function--this is not equal to the electron work function because the ion does not enter the metal when adsorbed. Consequently, adsorption leads to penetration by the ion of only part of the potential of the dipole layer.

The potential on an ion at any distance from the surface as a result of the field of the other ions and their images is

$$V(z) = e \sum_i \sum_j P_{ij}(\theta) \left(\frac{1}{r_{ij}^+} - \frac{1}{r_{ij}^-} \right) \quad (2)$$

where P_{ij} is the probability that an adsorbate exists at a lattice site, ij , in a square array. λ is the distance between the center of charge of an adsorbed ion and the image plane.

$$\begin{aligned} r_{ij}^+ &= (z - \lambda)^2 + r_{ij}^2 \\ r_{ij}^- &= (z + \lambda)^2 + r_{ij}^2 \end{aligned} \quad (3)$$

For the immobile case, $P_{ij}(\theta)$ vanishes except for the most probable sites, $2L_c/\theta_i^{1/2}$ apart, at which it is 1. In this case,

$$V(z) = V_{im} = \frac{2.25e\lambda^2 \theta_i^{3/2}}{L_c^3} \quad (4)$$

For mobile films: $P_{ij}(\theta) = \theta_i$ and $V(z) = V_m$ is given by

$$V_m = \frac{2.25e\lambda^2 \theta_i}{L_c^3} \quad (5)$$

Because $f = \left[\frac{V_\infty - V(z=\lambda)}{V_\infty} \right]^c$ we have for f :

$$f_{im} = 1 - \frac{2.25\lambda\theta_i^{1/2}}{\pi L_c} \quad (6)$$

and

$$f_m = 1 - \frac{2.25\lambda}{\pi L_c} \quad (7)$$

An expression for the intermediate case of partially mobile films can also be derived by noting that thermal energy will displace some of the ions from a well ordered array of the immobile film. This displacement results in an increase in potential ΔV in Equation (4) given by:

$$\Delta V = \frac{1}{N} \int_{V_{im}}^{\infty} \left(\frac{\theta_i \pi}{6L_c^2} \right) \left(2e\lambda^2 \right)^{2/3} V^{-2/3} \exp\left(\frac{-V}{kT}\right) dV \quad (8)$$

f_{im} is then modified to give for the case of partially mobile films

$$f = f_{im} - \frac{\Delta V}{V_\infty} \quad (9)$$

Equation (8) can only be integrated numerically.

Critique. - Barlow and Macdonald¹ have pointed out that the immobile array of Gadzuk and Carabateas is equivalent to what is usually considered to be a mobile array; whereas their mobile array is equivalent to the usual definition of localized films.

The values of f given in this paper neglect:

(1) The potential due to the image of the dipole induced in the ion which is being adsorbed at an empty site,

(2) All effects due to polarization of the adsorbed ions,

- (3) Possible redistribution effects of the existing lattice which may deform to accommodate the incoming ion.

Barlow and MacDonald have demonstrated in their recent paper that these effects are significant and deduce as a limiting case the formula of Gadzuk and Carabateas for an immobile and mobile array.

¹ Barlow and MacDonald, J. Appl. Phys. 37, 3471 (1966)
Paper 10, this series.

See Glossary for symbols not defined in text.

10 - PENETRATION PARAMETER FOR AN ADSORBED LAYER OF POLARIZABLE IONS

J. Appl. Phys. 37, 3471 (1966)

By J. Ross MacDonald and C. A. Barlow, Jr.

Review. - This paper contains calculations and discussion of the distinctions to be made between several different definitions of the penetration parameter f which were shown not to be equivalent when the ion polarizability α was not zero and when redistribution effects and interaction with self images could not be neglected. The ion array penetration parameter f is defined as follows; for ions of charge n :

$$f = \frac{-\Delta E_p}{n \Delta \phi} \quad (1)$$

where $\Delta \phi$ is the change in electron work function on adsorption and ΔE_p is the energy required to remove an adion from its equilibrium position in the array to infinity, minus that required when the surface coverage of adions approaches zero. Covalent contribution to ΔE_p are ignored and the array is assumed to be hexagonal and mobile. The simplest definition of f (let this be f_1) ignores possible redistribution effects in the adlayer when ions are removed or added and also does not consider the influence of the removed adions own image. Then:

$$f_1 = 1 - \frac{V_a}{V_\infty} \quad (2)$$

where V_a is the potential at the site of the missing adion and V_∞ is the potential arising from the adion-image array at an infinite distance from the adsorbing plane.

A more accurate definition of f includes the effect of the image of the induced dipole in the test ion:

$$f_2 = 1 - \frac{\Delta V_e}{V_\infty} \quad (3)$$

where

$$\Delta V_e = V_a + \frac{1}{2} [V_d - V_{do}] \quad (4)$$

V_d is the potential at the missing adion site arising from the image of the induced dipole of the test ion and $V_d = V_{do}$ when $\theta = 0$. Hence,

$$f_2 = f_1 - \frac{V_d - V_{do}}{2V_\infty} \quad (5)$$

Both f_1 and f_2 neglect possible rearrangement effects that might arise in the remaining adsorbate lattice when an ion is either adsorbed or desorbed. A third definition of f including the rearrangement energy for an array of polarizable adions is:

$$f_3 = \left[1 + f_2 - (V_d - V_{do})/2V - (N/V)(d\Delta V_i/dN) \right] / 2 \quad (6)$$

where N is the adsorbate surface density and V_i is the potential evaluated at an empty ion site; it includes induced polarization effects.

The next section of the paper is concerned with the evaluation of f_1 , f_2 and f_3 . A quantity f_1^0 , which is the value of f_1 when $\alpha = 0$, appears in the final expression for these quantities and is defined as:

$$f_1 = 1 - V_a^0/V_\infty^0 \quad (7)$$

where $V_\infty^0 = 4\pi Nne\bar{x}$ and \bar{x} is the perpendicular distance from the image plane to the charge centroid of an adion. V_a^0 , the value of V_a for $\alpha = 0$, was calculated from Grahame's "cut-off" model,¹ in which the discrete adion-image charges are smeared out into uniform sheets of charge having the same charge density as the discrete layers and having collinear circular vacancies of radius $r_0 = 4\pi d_1/s_1\sqrt{3}$. The quantity $s_1 \approx 11.034$ and comes from a lattice sum; d_1 is the nearest neighbour spacing. From these calculations:

$$f_1^0 = 1 + (2\pi R_1/s_1\sqrt{3}) - \left[(2\pi R_1/s_1\sqrt{3})^2 + 1 \right]^{1/2} \quad (8)$$

where $R_1 = d/r$. When $\alpha \neq 0$, f_1 may be calculated from Equation (2). V_∞ has been calculated in an earlier paper in this series.² V_a was calculated by resolving it into two components V_a^0 and V_{ap} where the latter is the potential contribution due to the induced dipole image array (less the ideal dipole at the central image position). An expression for f_1 is given by Barlow and MacDonald.

The more accurate array penetration parameter f_2 was obtained from Equation (5) in which the quantity $(V_d - V_{do})/2V_\infty$ was calculated in an earlier paper of these authors.² Finally f_3 was obtained by noting that $\Delta V_i = V_a^0 + V_{ap} + V_d - V_{do}$ and using the earlier calculated values of these quantities and of V_∞ and f_2 to elicit an expression for f_3 .

Plots of f_1 , f_2 and f_3 vs θ and R_1 are presented in Barlow and MacDonald's paper for various values of the parameters α and E_{ni} where E_{ni} is an effective surface field defined earlier.³ Increasing E_{ni} results in increased values of f for all three definitions of f , whereas for f_1 and f_2 , an increase in α results in a decline in f . At high surface coverages the same behavior occurs for f_2 ; at low coverages the reverse is true. The calculation for f_3 indicates that even for $\alpha = 0$ redistribution has a significant effect and that for $\alpha/r^3 \gg 1$, f_3 is markedly lower than f_2 .

Under some conditions f_1 , f_2 , and f_3 are negative; this implies that it requires more energy to remove an isolated ion from a metal than from an adsorbed array. This is a consequence of the surprising fact that for $\alpha \neq 0$, (V_a) may be greater than V_∞ . Using a normalizing factor Z equal to the ratio of the perpendicular distance from the surface divided by r , plots of the normalized quantity $V(Z)/V(\infty)$ vs Z/R_1 show that maxima in these curves occur for certain α values and that occurrence of the maximum requires higher values of α as coverage decreases. $V(Z)$ was calculated from the "cut-off" model.

Critique. - Barlow and MacDonald have carefully distinguished between a number of similar definitions of the penetration parameter and

have established expressions for them.

Because of the uncertainties about the value of the various parameters involved in these expressions, they are more suited to interpreting experimental ion desorption energy data than for making predictions about such energies. E_{ni} is only obtainable by comparing experiment with theory.

The authors point out that the ordered hexagonal array concept on which their calculations are based, probably loses its regularity below $\theta \sim 0.1$ so that this coverage represents a lower coverage limit for the applicability of the theory. A more serious limitation at higher coverage is posed by the uncertainty in the value of the ion charge n . From the work of Gurney⁴ it seems likely that n is a continuous function of coverage, so that failure to include the coverage dependence of n in the expressions for f will result in significant error. Barlow and MacDonald estimate an upper limit of $\theta \sim 0.7$ or 0.8 for the applicability of their theory although in view of the preceding considerations concerning n , this may be optimistic.

In spite of these criticisms, however, this work perhaps represents the most careful attempt to calculate the ion array penetration coefficient for a classical model of ions adsorbed in a hexagonal array.

¹ D. C. Grahame, Z. Elektrochem. 62, 264 (1958).

² J. R. MacDonald and C. A. Barlow, Jr., J. Chem. Phys. 44, 202 (1966) Paper 11, this series.

³ J. R. MacDonald and C. A. Barlow, Jr., J. Chem. Phys. 39, 412 (1963) Paper 9, this series.

⁴ R. W. Gurney, Phys. Rev. 47, 479 (1935).

11 - PROCESSES OF ADSORPTION AND DIFFUSION ON SOLID SURFACES

Trans. Far. Soc. 28, 333 (1932)

By J. E. Lennard-Jones

Review. - The dispersion theory of interaction between an adatom or molecule with a metal surface has been calculated by Lennard-Jones who used a classical model for the metal, assuming it to behave as a perfectly polarizable system, and a quantum mechanical model for the atom or molecule. The attraction between metal and adparticle is due to the attraction between the charges in the adparticle and their image equivalents in the metal.

Defining a Cartesian coordinate system centered on the adparticle of charge $+ne$ and distance z from the surface, then the image will be at $0, 0, -2z$ and the metal plane at $z = -z$. If z is large, the atom and its image may each be represented by N dipoles and the mutual potential energy is obtained from

$$v = -e^2/(2z)^3 \sum_{r,s} (x_r x_s + y_r y_s + 2z_r z_s),$$

where x_r and x_s are the coordinates of the adparticle and image electrons respectively. Note the energy of interaction between two dipoles \underline{M}_1 and \underline{M}_2 is given by

$$v = \frac{\underline{M}_1 \cdot \underline{M}_2}{r^3} - \frac{3(\underline{M}_1 \cdot \underline{r})(\underline{M}_2 \cdot \underline{r})}{r^5}$$

where \underline{M}_1 and \underline{M}_2 are the two dipoles and \underline{r} is the vector joining their centers. The potential energy of the atom due to its image is then

$$E_s = -e^2/(2z)^3 \int \psi^* \sum_{r,s} (x_r x_s + y_r y_s + 2z_r z_s) \psi d\tau_1 \dots d\tau_N$$

where $d\tau_N$ is the increment of volume and the wave function ψ for the whole atom is given by

$$\Psi = 1/(N!)^{1/2} \begin{vmatrix} u_1(1) & \dots & u_r(1) & \dots & u_n(1) \\ \vdots & & \vdots & & \vdots \\ u_1(N) & \dots & u_r(N) & \dots & u_n(N) \end{vmatrix}$$

in which u_n are the wave functions of the electrons in the atom and $u_r(s)$ represents the function obtained by substituting the coordinates of the s th electron in the r th wave function. Lennard-Jones was then able to show that

$$\int \Psi \sum_{r,s} (x_r x_s + y_r y_s + z_r z_s) \Psi d\tau_1 \dots d\tau_N = \overline{(x^2 + y^2 + z^2)}$$

where the last term is a mean value taken over the total electron space charge of the atom. The inert gas atoms are spherically symmetrical and $\overline{x^2} = \overline{y^2} = \overline{z^2} = R_o^2/3$ so

$$E = -e^2 \overline{R_o^2} / 6z^2$$

The quantity $\overline{R_o^2}$ may be obtained from the magnetic susceptibility equation:

$$\chi_s = - \left\{ L e^2 / 6 m c^2 \right\} \overline{r^2}$$

where χ_s is the susceptibility per gram atom, L is Avogadro's number, m is the mass of the electron and c is the velocity of light.

Critique. - The Lennard-Jones treatment is semi-classical. Although it treats the atom as a quantum-mechanical system, it fails to allow for the quantum mechanical behaviour of the conduction electrons in the metal. The model also fails to take into account the fact that the electrons in the metal have a finite relaxation time and cannot keep an electrical image in phase with the motions of the electrons in a neighboring molecule. Bardeen¹ has estimated that when both metal and molecule are treated quantum mechanically, the interaction is still proportional to r^{-3} , but is only about one half of that estimated by Lennard-Jones. The discrepancy arises

because the Lennard-Jones treatment involves neglect of a term in the kinetic energy of the system of molecule plus metal. Bardeen also noted that a numerical error occurs in Lennard-Jones expression for the interaction between a molecule and a metal: The correct expression is one-half of Lennard-Jones's.

¹ J. Bardeen, Phys. Rev. 58, 727 (1940).

12 - THE INTERACTION BETWEEN A MOLECULE AND A METAL SURFACE

Phys. Rev. 61, 65 (1942)

By E. J. R. Prosen and R. G. Sachs

Review. - Prosen and Sachs have used a second order perturbation treatment to calculate the interaction between a metal surface and a molecule. The interaction arises from the field of the instantaneous dipole of the molecule which acts on electron and positive ions of the metal. This mechanism does not involve charge exchange between the metal and substrate and is hence applicable to physical adsorption.

Since the average value of the dipole of the molecule is zero, the first order perturbation energy vanishes and the energy, E , of interaction of the molecule and metal will be given by the second order term:

$$E_s = \sum_m \frac{V_{om} V_{mo}}{E_o - E_m} \quad (1)$$

where $V_{om} = V_{mo}^*$ are the matrix elements given by

$$V_{om} = \int \psi_o^* V \psi_m dr$$

and ψ_o and ψ_m are wave functions of the system of molecule plus metal in the initial state and in the m th excited state, respectively. The quantities E_o and E_m are the energies of the states ψ_o and ψ_m , while V is the potential energy of interaction given by the sum

$$V = V^x + V^y + V^z$$

where

$$V^x = M^x H^x, \quad V^y = M^y H^y, \quad V^z = M^z H^z.$$

The components of the dipole moment of the molecule are M^x , M^y , M^z . The quantities H^x etc. depend only on the position of the center of gravity of the molecule and the positions of the electrons and positive ions in the metal.

The zero th approximation of ψ_o and ψ_m are given by the simple product of molecular wave functions, ϕ and metal wave functions χ :

$$\psi_o = \phi_o \chi_o, \psi_m = \phi_i \chi_k$$

so that

$$\begin{aligned} V_{om}^x &= \int \phi_o^* M^x \phi_j dr \int \chi_o^* H^x \chi_k dr \\ &= M_{oj}^x H_{ok}^x \end{aligned} \quad (2)$$

Similar expressions exist for V_{om}^y and V_{om}^z . Combining equations (1) and (2) gives

$$E = \sum_{x, jk} \frac{M_{oj}^x M_{jo}^x H_{ok}^x H_{ko}^x}{E_{oo} - E_{jk}}$$

where the summation is to take place over x, y, z and over all states j of the molecule and all states k of the metal. Note that

$$\begin{aligned} E_{oo} &= E_o + E_o' \\ E_{jk} &= E_j + E_k' \end{aligned}$$

where E_o and E_j refer to the energies of the ground and j the states of the molecule and E_o' , E_k' refer to the initial and k th states of the metal. The difference $E_o' - E_k'$ may be neglected so that E may be expressed as:

$$E = \sum_{x, j, \backslash o} \frac{M_{oj}^x M_{jo}^x}{E_o - E_j} \left(\sum_k H_{ok}^x H_{ko}^x \right)$$

We note that

$$a_{xx} = -2 \sum_j \frac{M_{oj}^x M_{jo}^x}{E_o - E_j}$$

with similar expressions for a_{yy} and a_{zz} . These quantities are the diagonal elements of the polarizability tensor of the molecule. Averaging

overall orientations of the molecule we have

$$E = -1/2 a \sum_{x,k} H_{ok}^x H_{ko}^x \quad (3)$$

with $a = \langle a_{xx} \rangle_{av} = \langle a_{yy} \rangle_{av} = \langle a_{zz} \rangle_{av}$

Now H^x etc. are terms corresponding to the interaction of the dipole field of the molecule with each electron and positive ion in the metal. It was assumed that the electron density was low enough so that the Fermi degeneracy could be neglected; moreover, the interaction between electrons was neglected. After these assumptions and further mathematical manipulation we have

$$\sum_k H_{ok}^x H_{ko}^x = \frac{\rho_e^2 \pi}{2z}$$

$$\sum_k H_{ok}^y H_{ko}^y = \sum_k H_{ok}^z H_{ko}^z = \frac{\rho_e^2 \pi}{4z}$$

where ρ_e is the number of electrons per unit volume in the metal and z is the perpendicular distance between the molecule and metal; hence, Equation (3) becomes

$$E = \frac{-a\pi\rho_e^2}{2z}$$

The Fermi degeneracy was taken into account by anti-symmetrizing the metal wave functions so that electrons cannot make transitions to those states already occupied. When this is done,

$$E = \frac{-a e^2 \pi k_m \log 2k_m z}{(2\pi)^3 z^2}$$

where the factor πk_m^2 is the area of that cross section of the surface of maximum energy in momentum space which passes through the origin and is perpendicular to the x axis.

Prosen and Sachs considered the effect of electron-electron interactions and concluded that z should be less than $[\Delta E / 2\pi \rho_e^2]^{1/2}$ if these correlation effects were to be negligible compared to E . Note that ΔE is some average difference in energy between levels in the adsorbate molecule. For metals this means that the critical value of z is of the order of a Bohr radius. For the perturbation treatment to be justified, z must be large enough to render the overlap between the molecular and metal wave functions small. Hence, the range of z for which the above treatment is valid is small for metals. However, if ρ is lower as in semiconductors or metals at high temperatures, the range of z for which this treatment is valid is much larger.

Critique. - The Prosen-Sachs treatment of metal-adsorbate dispersion energies involves a perturbation approach which neglects electron-electron interactions. This neglect is more serious for metals than for semiconductors so that the theory is more easily applicable to these latter substrates than to metals. There exists only a narrow range of substrate / adsorbate distances for which the overlap between the molecular and metal wave functions is sufficiently small to justify a perturbation treatment and for which simultaneously the electron-electron interaction is negligible. The range is wider for semiconductors than for metals because of the lower density of conduction electrons in semiconductors. Because this treatment is valid in the range of small r it is more important in the calculation of heats of adsorption than say the theory of Margenau and Pollard¹ which applies for larger values of r .

In order to calculate the dispersion heat of adsorption, the value of r is required² for the distance between the center of the adatom to a plane surface which marks a discontinuous transition from a vacuum to a region with the properties of the interior of the bulk. According to de Boer³ this value of r is indefinite by a factor of nearly two near the equilibrium distance of the adsorbed atom so that the calculated dispersion energy

may be uncertain to within an order of magnitude.

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- ¹ H. Margenau and W. G. Pollard, Phys. Rev. 60, 128, (1941)
 - ² Physical Adsorption of Gases by D. M. Young and A. D. Crowell, Butterworths, Washington, D. C. 1962.
 - ³ J. H. de Boer Advances in Catalysis 8, 17 (1956).

WORK FUNCTION CALCULATIONS

13 - VAPOUR PRESSURES, EVAPORATION, CONDENSATION AND ADSORPTION

J. Am. Chem. Soc., 54, 2798 (1932)

By I. Langmuir

Review. - Langmuir's contribution to the theory of work function change, ion and neutral desorption energy is made in the form of a semi-empirical procedure which rests upon experimentally determined values of the atom evaporation rate. The theories underlying Langmuir's 1933 paper are as follows:

First, he assumed that the mechanism by which equilibrium is established between vapor and bulk phase of liquids or solids was identical to that for adsorbate and substrate equilibrium. From these considerations, five important equations were derived:

$$\tau = \sigma/q \quad (1)$$

$$p = A T^{3/2} \exp (-b/T) \quad (2)$$

$$\delta/\delta_o = C_1 T^{-1/2} \exp (b/T) \quad (3)$$

$$\theta = C_2 S P T_M^{3/2} \exp (b/T) \quad (4)$$

$$q/\theta = C_3 T \exp (-b/T) \quad (5)$$

where q is the evaporation rate from a completely covered surface, δ is the distance travelled by an adparticle before evaporating and δ_o is the distance between nearest atoms in the substrate; S is the condensation coefficient, θ represents relative surface coverage, τ the lifetime of an adsorbed molecule, A is a universal constant, b is approximately a direct measure of adsorption energy and σ is surface coverage of adsorbate ($\sigma = \sigma_1$, when $\theta = 1$).

Secondly, by employing the Gibb's adsorption equation, a two-dimensional version of the van der Waals equation, and a two-dimensional version of the Clausius virial equation, Langmuir was able to derive an

expression for the spreading pressure Π of the adsorbed layer in terms of the average effective dipole moment M on the adparticles, thus:

$$\Pi = +3.34 \sigma^{5/2} M^2 + 1.53 \times 10^{-5} \sigma^2 T^{1/3} M^{4/3} \mathcal{I} \quad (6)$$

where \mathcal{I} is an integral which is a function of M , T , σ , and θ ; and Π is that part of the spreading pressure due to the repulsion of the dipoles. Π was obtained from Taylor's experimental work for cesium atom desorption from tungsten so that M was obtainable as a function of surface coverage. Once M was obtained, it was possible to calculate the work function change, $\Delta\phi$, from the Helmholtz equation:

$$\Delta\phi = 2\pi M \sigma \quad (7)$$

$$\ln(2q_p) = \ln q_a + \frac{e}{kT} (\phi_w - V_I - \Delta\phi) \quad (8)$$

(Saha Equation)

where ϕ_w is the work function of clean tungsten. By using the Saha Equation, for ion evaporation it was also possible to calculate rates of ion desorption of cesium from tungsten from calculated values of $\Delta\phi$. The activation energy of ion desorption is thus $\phi_w - V_I - \Delta\phi$ less than the neutral desorption energy. Equation (5) gives rate of atom evaporation in terms of the heat of adsorption so that if b could be calculated it would be possible to calculate: (1) rates of atom evaporation, (2) rates of ion evaporation, (3) rates of electron emission for comparison with experimental data. Unfortunately, Langmuir was not able to calculate b which is a function of substrate, its surface geometry and adsorbate coverage.

Critique, - Langmuir was able to predict the variation of work function up to $\theta = 0.5$ with the aid of experimentally determined values of the neutral atom desorption rate. Beyond $\theta = 0.5$ his theoretical work function values were less than his experimental ones by an amount which increased with coverage. Moreover, the theoretical curves did not exhibit the maximum which the experimental ones show.

Langmuir's model is a classical one and as such suffers from the same defect¹ as other classical treatments in which the adsorbed particles are treated as independent classical elements. The model defects only become manifest at high coverages where the individual adsorbed particles coalesce into a two-dimensional macrocrystal in which the adsorbate valence electrons occupy positions within a new adsorbate valence band. Under these circumstances the classical treatment employed by Langmuir and others is inadequate to account for work function coverage dependencies.

¹ J. Ross MacDonald and C. A. Barlow, Jr., J. Chem. Phys. 39, 421 (1963) Paper 15, 16 this series.

14 - CORRELATION OF EMISSION PROCESSES FOR ADSORBED ALKALI FILMS ON METAL SURFACES

J. Appl. Phys. 35, 2589 (1964)

By. N. D. Rasor and C. Warner

Review. - Rasor and Warner used an analytic model similar to that of Langmuir¹ insofar as the ion cores of the adsorbed particles, to a first approximation, can be considered as classical spheres resting on a conducting plane and occupying sites in an array determined by the substrate surface structure. Gurney² pointed out that as an adsorbate atom approaches a metal the valence level of the atom (if $V_I \sim \emptyset$) will broaden into a band of states common to both metal and atom. The extent of this broadening, Δ , depends on the distance of the adsorbate atom ion core from the surface. If this is small enough so that $\Delta \ll kT$, the valence energy band of the atom is sharp and ions and neutrals exist as separate states on the surface. The relative probability of atomic and ionic states is given by:

$$\frac{\theta_a}{\theta_i} = y \exp \left[\frac{-\Delta E}{kT} \right] \quad (1)$$

where ΔE is the mean energy difference between these states on the surface, and $y = 2j$ for j highly localized energy levels in the valence band; j is the number of highly localized energy levels in the valence band. The work function change due to adsorption was expressed as:

$$\frac{\Delta \phi}{e} = 2\pi \sigma_0 (M_i \theta_i + M_a \theta_a) \quad (2)$$

where σ_0 is the surface site density and M the dipole moment associated with a surface ion or atom. Owing to depolarization M is related to the moment at zero coverage by:

$$M_i = M_{i0} - \alpha_i F, \quad M_a = M_{a0} - \alpha_a F \quad (3)$$

Consideration of a simple thermodynamic cycle yielded:

$$\Delta E + E_a + V_I - E_p - \phi = 0 \quad (4)$$

$$\Delta E_o + E_{ao} + V_I - E_{po} - \phi_o = 0 \quad (5)$$

where ΔE is the difference in bonding energy between the adsorbed ion and adsorbed atom, E_a is the atom adsorption energy, V_I , its ionization potential, E_p , the ion desorption energy and ϕ the substrate work function. Equation (5) contains the same quantities at zero surface coverage. The ion array penetration coefficient, f , is defined as:

$$f = \frac{E_p - E_{po}}{\Delta\phi} \quad (6)$$

Rasor and Warner expressed the depolarization field F as:

$$F = (1-f) \frac{\Delta\phi}{er_i} \quad (7)$$

where r_i is the ionic radius. By combining the above equations, using $\theta = \theta_i + \theta_a$ and noting that $\Delta E = \Delta E_o - (1-f) \Delta\phi + \Delta E_a$ where $\Delta E_a = E_a - E_{ao}$, the final implicit expression obtained for $\Delta\phi$ was

$$\Delta\phi = \frac{4\pi e^2 \sigma_o \left\{ 1 - \left[a_i (1-f)/2 e^2 r_i \right] \Delta\phi \right\} \theta}{1 + y \exp (\Delta E/kT)} \left[1 + \frac{M_a \theta_a}{M_i \theta_i} \right] \quad (8)$$

f may be calculated from geometric considerations and ΔE_o depends on E_{ao} and E_{po} both of which are estimated below. Calculation of $\Delta\phi$ requires some assumptions to be made about M_a and ΔE_a . Comparison of the experimental with theoretically predicted values indicates that ΔE_a and $(M_a/M_i) (\theta_a/\theta_i)$ may be neglected. M_{io} was assumed to be given by $M_{io} = 2 er_i$. E_{ao} was estimated from a semiempirical formula:

$$E_{ao} = b (h_a h_o)^{1/2} \quad (9)$$

where $0.5 < b < 1$, h_a is the heat of vaporization of the bulk adsorbate and h_o that of the substrate. An attempt to express E_{ao} in terms of ϕ_m was also made and the semiempirical relation:

$$E_{ao} \sim 0.34 + 0.3 \phi_m \quad (10)$$

was obtained. For the noble metals, the term $0.7 \phi_m$ was found to be more appropriate than $0.30 \phi_m$. By noting that experimentally, h_o is approximately proportional to substrate work function ϕ_m , Equation (9) may be used to predict E_{ao} . A calculation based on the classical image forces on the valence electron, the ion core, and a free electron gave the following relation between ϕ_m and E_{ao} in terms of the electronic charge e , and the ionic radius r_i .

$$E_{ao} = \frac{e^2}{8r_i} \ln \left[1 + \frac{8r_i}{e^2} \phi_m \right] \quad (11)$$

Critique. - Whether or not Rasor and Warner can use their Equation (1) for calculating θ_i in terms of θ_a depends on the width of the broadened valence band level Δ compared to kT . If $\Delta < kT$, then Equation (1) may be used. Δ was estimated from $\Delta \sim h/2\pi\Delta t$ where Δt is the lifetime of an atomic state calculated from $1/\Delta t = n \delta \exp(-cd)$ where n is the frequency of oscillation of the electron in the potential well of the ion core, δ is the fraction of encounters of the ion core with the well boundary in the direction of the surface $10^{-2} < \delta < 1$ and d is the barrier width $cd \sim 1$. From these values $3 \times 10^{-15} < \Delta t < 3 \times 10^{-13}$ seconds and this in turn implies that $0.002 < \Delta < 0.2$ eV so that if $kT \sim 0.2$ eV, $\Delta < kT$ and Equation (1) will be valid.

Because of the sharp dependence of Δ on c and d small errors in the estimates of these quantities can obviate the validity Equation (1); moreover, this relation will not hold at room temperature for which $kT \sim 0.002$ eV. In contrast to Rasor and Warner, Gomer³ and Schmidt have estimated a very much larger broadening for k adsorbed on W ($\Delta \sim 3$ eV) and Bennett⁴ and Falicor using a perturbation quantum mechanical approach have substantiated Gomer's estimate. Gadzuk has also calculated Δ by a similar method to

Bennett and Falicor. Gadzuk's⁵ value of Δ is about 1 eV. In view of these calculations, Equation (1) is not expected to be useful. In addition, as in the case of Gadzuk's theory, the temperature dependence predicted by the model of Rasor and Warner is not in accord with experiment.

- ¹ I. Langmuir, J. Am. Chem. Soc. 54, 2798 (1932). Paper 13, this series.
- ² R. W. Gurney, Phys. Rev. 47, 479 (1935).
- ³ R. Gomer and L. D. Schmidt, J. Chem. Phys. 42, 3573 (1965).
- ⁴ A. J. Bennett and L. M. Falicor, Phys. Rev. 151, 512 (1966).
- ⁵ J. W. Gadzuk, Surface Sci. 6, 133 (1967).

15 - WORK FUNCTION CHANGE ON MONOLAYER ADSORPTION

J. Chem. Phys. 39, 412 (1963)

By J. Ross MacDonald and C. A. Barlow, Jr.

Review. - MacDonald and Barlow have developed a semiempirical theory of work function change which employs the concepts of effective polarizing field F_1 and effective orienting field F_2 . F_1 is a field which would produce the same polarizing effect as that produced by covalent bonding, nonpolar van der Waals etc., while F_2 is a fictitious normal field which would produce the actual time average orientation of the permanent dipoles perpendicular to the adsorbent surface. F_1 is the sum of two fields:

$$F_1 = F_{nl} + F_{eff} \quad (1)$$

F_{nl} is a surface field that is normal to the surface and uniform through an adsorbate surface layer of thickness t . It is a field that is independent of the average surface charge density of both the adsorbate q_a and the adsorbent q . F_{eff} is the field at the position of the adsorbed particle. F_{eff} is constant through the thickness t and arises directly from the average charge on the electrode and from the depolarizing effect of all the surrounding polarized units.

$$F_{eff} = 4\pi(q + q_a) + F_d \quad (2)$$

The depolarizing field F_d is obtained by summing over all discrete dipoles and is given by:

$$F_d = - \left[\alpha F_1 + \langle M(F_2) \rangle \right] \Omega \delta (\theta N_s)^{3/2} \quad (3)$$

where $\delta = 1$ for the mobile case and $\theta^{-1/2}$ for the immobile. Ω is very close to 9 for both square and hexagonal arrays of adsorbate species on the surface. The average induced polarization due to F_1 is P_1 and is

related to the maximum possible number of adsorbed particles per unit area N_s , the relative coverage θ , and the polarizability of the adsorbed species a by:

$$P_1 = N_s a F_1 \theta / d \quad (4)$$

The effective field leading to permanent dipole orientation perpendicular to the adsorbent surface F_2 is also related to F_{eff}

$$F_2 = F_{n2} + n_r^{-2} F_{\text{eff}} \quad (5)$$

The n_r^{-2} factor is introduced because the effect on a given dipole of F_{eff} is screened out by the electronic contribution to the high-frequency dielectric constant. The polarization resulting from F_2 is given by:

$$P_2 = (N_s a \theta / t) \langle M(F_2) \rangle \quad (6)$$

where $\langle M(F_2) \rangle$ is the time averaged perpendicular component of permanent dipole when the average orienting field is F_2 .

If q and q_a are unchanged by adsorption the work function change, $\Delta\phi$, on adsorption is:

$$\Delta\phi = -4\pi t P \quad (7)$$

where $P = P_1 + P_2$. Combining Equations (1) through (7), the work function change as a function of coverage is derived.

$$\Delta\phi = \frac{-4\pi\theta N_s}{1 + \alpha \Omega \delta (\theta N_s)^{3/2}} \left[4\pi\alpha(q + q_a) + a F_{n1} + \langle M(F_2) \rangle \right] \quad (8)$$

This formulation does not hold when the dipoles are formed by adsorbed ions and their images in the conducting adsorbent. In this case, $\langle M(F_2) \rangle$ is replaced by $2ner$, where $2r$ is the distance between ion and image. Application of Gauss's law leads to:

$$\phi_1 = 4\pi(q + q_a) d - 4\pi q_a r - 4\pi P_1 D \quad (13)$$

where n is the effective valence of an adsorbed entity,

from which:

$$\phi = -4\pi\theta N_s a \left\{ \frac{4\pi(q + q_a) + F_{nl}}{\epsilon_{eff}} \right\} - 4\pi\theta N_s (ner) \left\{ \frac{2}{\epsilon_{eff}} - 1 - \left(\frac{d}{r} \right) \right\} \quad (14)$$

where $\epsilon_{eff} = 1 + a\Omega\delta(\theta N_s)^{3/2}$

In the above treatment of work function change, dipole imaging has been neglected; moreover, the ion-image dipoles are treated as ideal.

Note: The corrections which Barlow and MacDonald made to this paper in J. Chem. Phys. 44, 202, (1966), have been incorporated into the above equations.

Critique. - This paper contains an approximate classical treatment of the work function change due to adsorption in which it has been assumed that the image dipoles are assumed to be ideal and in which the imaging in the metal of permanent and induced dipoles have been neglected. Most of the deficiencies of this theory have been pointed out by the authors. Thus the effect of thermal motion in the plane of the adsorbent has been neglected and the only temperature effect on work function is introduced via the Langevin function which contains the permanent dipole term. Additionally, the theory only applies when the adsorbate is adsorbed into a single adsorption state. This may be satisfactory for alkali and alkali-metal adsorption but is clearly unsatisfactory for electronegative adsorption in which adsorption into a multiplicity of states is usually the rule rather than the exception. Although the electropositive adsorbates do not exhibit multiple binding modes, it seems likely that they possess variable charge numbers when adsorbed and that the residual charge on the adsorbate atom is a function of coverage. At low coverages, the binding is probably very nearly ionic for adsorbates such as potassium and cesium while at high coverages it is probably only slightly polar. A consequence of variable, nonintegral charge number n , is that a , the adsorbed particle polarizability, is also coverage dependent. Since the present theory does not predict how n and a vary with θ , it is unlikely to account for work function changes over a wide coverage interval even for

electropositive adsorbates.

The employment in the theory of F_{n1} and F_{n2} , which are not calculable except by reference to experiment, precludes the possibility of predicting the value of $\Delta\phi$ at a particular coverage.

The utility of this theory may, however, exist in its capacity to interpret experimentally observed work function changes.

¹ R. W. Gurney, Phys. Rev. 47, 479 (1935). Paper 7, this series.

16 - THEORY OF WORK FUNCTION CHANGE ON ADSORPTION OF POLARIZABLE IONS

J. Chem. Phys. 44, 202 (1966)

By J. Ross Macdonald and C. A. Barlow, Jr.

Review. - In this paper the authors have corrected an earlier semiempirical formulation of the work function change¹ resulting from the adsorption of an array of ions or molecules. They have extended this treatment to real, instead of ideal image dipoles and have also considered the effect of the images of the dipoles induced in the adions. Many of the symbols used in this review paper are defined in papers 10 and 15 of this series.

From Gauss's law and Equation (33) of reference 1 is derived the expression $V_{\infty} = 4\pi q_a r + 4\pi P_1 t + 4\pi \theta N_s \langle M/F_2 \rangle$ where V_{∞} is the contact potential due to adsorption. Let $V_{\infty}^0 = 4\pi q_a r$, then $V_{\infty} = V_{\infty}^0 + 4\pi \theta N_s a F_1 = 4\pi \theta N_s \langle M(F_2) \rangle$. Note: F_1 and F_2 were defined in ref. 1. F_d is recalculated here for polarizable ions. The depolarizing field F_d was calculated by considering an infinite plane array of adsorbed elements with one element removed. All other physical properties of the layer were assumed unchanged by the removal. F_d is the field acting at the charge centroid of the removed element and was calculated by Barlow and Macdonald by resolving F_d into five components: F_{di} ; $i = 1, 2, 3, 4, 5$. They are:

$$F_{d1} = \frac{-ne}{4r^2}$$

due to image charge of removed element.

$$F_{d2} = \frac{aF_1 + \langle M(F_2) \rangle}{4r^3}$$

due to image dipoles of removed element.

$$F_{d3} = - \left[aF_1 + \langle M(F_2) \rangle \right] s_1 d^{-3}$$

due to contributions from all other surrounding dipoles.

$$F_{d4} = - \frac{V_{\infty}^0}{2r} \left[0.9117 + (2\pi R_1 / \sqrt{3} s_1)^2 \right]^{-1/2}$$

due to surrounding nonideal dipoles formed by the adion charges and their images; and finally:

$$F_{d5} = - \left(\frac{8\pi^3}{3^{3/2} 2} \right) \left[\frac{aF_1 + \langle M(F_2) \rangle}{r^3} + \left(\frac{2\pi R_1}{\sqrt{3} s_1} \right)^2 \right]^{-3/2}$$

due to the images of all surrounding ideal dipoles. Note that in F_{d4} , V_{∞}^0 is defined by $V_{\infty}^0 = 4\pi\theta N_s ner$ and $R_1 = d/r$ where d is the nearest neighbor spacing of discrete elements.

An equation for V_{∞} may be derived from these quantities but owing to the dependence of $\langle M \rangle$ on F_2 is not explicit.

In this paper Barlow and Macdonald correct an earlier expression¹ for the work function change due to adsorption of polarizable ions and the result is:

$$-\Delta\phi = V_{\infty} = \frac{4\pi\theta N_s}{F_{eff}} \left[aF_{nl} + (2 - F_{eff}) ner \right] \quad (1)$$

An explicit result superior to that in Equation (1) is obtainable from the Equations preceding (1) if the permanent dipole of the adion is assumed to be zero. In this case:

$$V = V_{\infty}^0 \left[1 - g(R_1) \right] \quad (2)$$

where

$$g(R_1) = \frac{1}{2F_1} \left(\frac{a}{r^3} \right) \left[\frac{(8\pi/\sqrt{3})R_1^{-2}}{\left\{ 0.9117 + (2\pi R_1/\sqrt{3} s_1)^2 \right\}^{1/2}} + \frac{1}{2} - 2 \left(\frac{r}{ne} \right) \left(rF_{nl} \right) \right] \quad (3)$$

and

$$F_1 = 1 + \left(\frac{a}{r^3} \right) \left\{ s_1 R_1^{-3} - 1/4 + (8\pi^3/3)^{3/2} s_1^2 \left[1 + (2\pi R_1 \sqrt{3} s_1)^2 \right]^{-3/2} \right\} \quad (4)$$

¹ J. Ross Macdonald and C. A. Barlow, J. Chem. Phys. 39, 412 (1963) (Paper 15, this review series)

Critique. - This paper represents an added degree of sophistication to the theory presented earlier.¹ The adsorbed ions and their images are no longer treated as ideal dipoles and additionally, the images of induced dipoles are explicitly considered.

The general critique applied earlier to ref. 1 also applies to the theory incorporating the above refinements. As with the earlier theory, the utility of this one lies in fitting the experimental with the theoretical in order to obtain values of the various parameters appearing in the expression for work function change. The fit obtained was found to be insensitive to choice of E_{ni} . Unfortunately, the experimentally determined values of a and r were considerably smaller than the likely values if the data was fitted over the whole θ range. However, reasonable combinations of the parameters n , r and a are obtained if fit is restricted to the range $0 < \theta < 0.6$.

¹ J. Ross Macdonald and C. A. Barlow, Jr., J. Chem. Phys. 39, 412 (1963). (Paper 15, this review series).

17 - WORK FUNCTION VARIATION OF METALS COATED BY METALLIC FILMS

J. Appl. Phys. 33, 67 (1962)

By E. P. Gyftopoulos and J. D. Levine

Review. - Gyftopoulos and Levine have employed a phenomenological approach to develop an expression for the work function change, $\Delta\phi$, due to adsorption. $\Delta\phi$ was expressed in terms of the work functions of the metallic substrate, ϕ_m , and adsorbate, ϕ_f , and in terms of the adsorbate polarizability α , the number of sites available for adatom occupancy per unit substrate area to form a monolayer σ_0 , a dielectric constant ϵ_0 , the distance between the centers of the adsorbate atom and the nearest substrate atom, R , the angle 2β between the directions along R for two diagonally opposite pairs of substrate, adsorbate atoms arranged in a square lattice, and the relative surface coverage θ .

No attempt was made to establish the dependence of $\Delta\phi$ on temperature and a dynamic equilibrium situation was assumed for all degrees of coverage.

It was also assumed that the work function barrier $\Delta\phi$ could be resolved into a dipole barrier, $d(\theta)$, due to a surface double layer and into an electronegativity barrier, $e(\theta)$, the functional form of which was fixed by considering experimentally known boundary conditions for the work function behavior in the coverage range $0 < \theta < 1$. These boundary conditions may be expressed analytically as follows:

$$e(0) = \phi_m \quad ; \quad \left. \frac{de(\theta)}{d\theta} \right|_{\theta=0} = 0 \quad (1)$$

where ϕ_m is the effective work function of the substrate. It is observed experimentally that for a fully covered surface, the effective work function is that of the adsorbate, ϕ_f . This is expressed:

$$e(1) = \phi_f \quad ; \quad \left. \frac{de(\theta)}{d\theta} \right|_{\theta=1} = 0 \quad (2)$$

The expression for the electronegativity barrier, found by expanding $e(\theta)$ in a power series and choosing the simplest polynomial consistent with Equations (1) and (2), is found to be

$$e(\theta) = \phi_f + (\phi_m - \phi_f) G(\theta) \quad (3)$$

where $G(\theta)$ is a shape factor chosen to fit the experimental results. For this paper it is chosen to be:

$$G(\theta) = 1 - 3\theta^2 + 2\theta^3 \quad (4)$$

The dipole moment is derived directly from the electronegativity barrier, using Pauling's statement that the dipole moment of a molecule of two dissimilar atoms is related to their difference in electronegativity. Using the Gordy-Thomas relation between electronegativity and work function of a pure metal for the composite surface and Equation (4), the effective dipole moment was related to the shape factor $G(\theta)$ via:

$$M(\theta) = M_o G(\theta) \quad (5)$$

where M_o is the dipole moment of a single adsorbate substrate dipole at zero coverage. The effective dipole moment $M_e(\theta)$ is diminished by depolarization and Gyftopoulos and Levine used Topping's formula to account for this:

$$M_e(\theta) = M(\theta) / (1 + 9\alpha\sigma_o^{3/2} \theta^{3/2} / 4\pi\epsilon_o) \quad (6)$$

$d(\theta)$, the dipole barrier is then,

$$d(\theta) = \frac{-4\pi M_e(\theta) \sigma_o \theta}{4\pi\epsilon_o} = \frac{-\theta G(\theta) \sigma_o M_o}{\epsilon_o \left[1 + 9 \alpha \sigma_o^{3/2} \theta^{3/2} / 4\pi\epsilon_o \right]} \quad (7)$$

The dipole moment at zero coverage M_o depends on adsorbate and substrate material as well as on crystallographic structure of the surface. M_o was expressed as the sum of the four perpendicular components of the dipole moments M_{fm} formed between an adsorbate atom and each of

its four nearest substrate neighbors resting in a square lattice beneath the adatom. M_{fm} was evaluated in terms of the differences in electronegativities of the adsorbate x_f and the substrate x_m . The resulting expression is:

$$M_{fm} = \frac{K (x_m - x_f)}{1 + a / 4\pi\epsilon_0 R^3} \quad (8)$$

where R is the sum of the adsorbate and substrate covalent radii and $K = 3.83 \times 10^{-30}$ coul-m/v is deduced from existing data on the relationship between electronegativity and molecular dipole moment. The denominator in Equation (8) has been included to account for self-depolarization. Using the effective work function

$$\phi_e(\theta) = e(\theta) + d(\theta)$$

and the expressions for $e(\theta)$ and $d(\theta)$, yields the desired expression for the variation of work function with coverage:

$$\frac{\Delta\phi}{\phi_m - \phi_f} = 1 - G(\theta) \left[1 - \frac{0.765 \times 10^{-18} \sigma_0 \theta \cos\beta}{\left\{ 1 + \left(\frac{a}{4\pi\epsilon_0 R^3} \right) \right\} \left\{ 1 + \frac{9a\sigma_0^{3/2} \theta^{3/2}}{4\pi\epsilon_0} \right\}} \right] \quad (9)$$

where $\Delta\phi = \phi_m - \phi_e(\theta)$

Equation (9) predicts either a maximum or a plateau in the variation of ϕ_e with θ when $\theta < 1$ for some adsorbate-substrate combinations. A more rapid change of ϕ_e with θ and a greater value of $\Delta\phi$ are predicted for the more densely packed crystallographic planes.

Critique. - Since the calculation of $\Delta\phi$ by Gyftopoulos and Levine requires prior knowledge of ϕ_f and ϕ_m , the model developed by them predicts only the shape of the $\Delta\phi$ vs θ curve. It makes no prediction about the magnitude of $\Delta\phi$ at $\theta = 1$; neither does it offer any clues about the temperature dependence of $\Delta\phi$ at constant θ .

Good agreement with Langmuir's data was obtained if his measured

value of $\sigma_f = 4.8 \times 10^{14}$ cesium atoms/cm² was used. However, this value is an apparent one and is greater than the actual density by the surface roughness factor which is roughly 1.3. Calculated values of $\Delta\phi$ vs θ for adsorption of cesium on the (100), (110) and a rough plane of tungsten do not exhibit the maximum which is now a well established feature of this system for the (110), (211), (100) and (111) planes.² The experimental results of reference 2 do suggest, though, that the maximum is more pronounced for the (110) and (211) planes than for the (100) and (111). In spite of the absence of a maximum in Gyftopoulos and Levine's calculations for cesium on tungsten, Equation (8) of Section I will yield a maximum if an appropriate choice of physically reasonable values of α , R , etc. is made.

The authors of this review are dubious about the assertion that ϕ can be divided into a dipole and an electronegativity barrier. We feel that $\Delta\phi$ can probably be expressed in terms of the dipole barrier or perhaps in terms of the electronegativity barrier but that it is not equal to the sum of both.

¹ I. Langmuir and J. B. Taylor, Phys. Rev. 44, 423 (1933).
Paper 13, this series.

² R. Gomer and L. D. Schmidt, J. Chem. Phys. 45, 1605 (1966)

18- THEORY OF ELECTRICAL DOUBLE LAYERS IN ADSORBED FILMS

Phys. Rev. 47, 479 (1935)

By R. W. Gurney

Review. - Gurney discussed the conditions under which ionic, covalent and polar bonds are formed, in terms of the work function of the metal, ϕ , the ionization potential, V_I , and the extent of broadening of the valence level of the adsorbate atom as it approaches the metal surface. He pointed out that if the adsorbate atom possesses an allowed energy level near the Fermi level of the metal, this level will broaden into a band of states as the atom moves closer to the solid. Because the potential barrier between the ion cores of the adsorbed particles is like the barrier between the ion cores of bulk atoms, that is, transparent to the free electrons of the metal, an equilibrium concentration of electrons is immediately established in the vicinity of the adsorbate ion core. Whether or not this concentration is sufficient to neutralize the charge on the ion core depends on the relative positions of the metal Fermi level and the center of the new band of states associated with the adsorbate particle. Univalent adsorbates require coincidence of the Fermi and valence levels for neutrality because only in this case is the single charge on the adsorbate ion core balanced by the single electron present in the half-filled adsorbate band. Divalent adsorbate atoms acquire a single positive charge when $V_I = \phi$, because the half-filled adsorbate band is clearly insufficient to neutralize the doubly charged ion core of the adsorbate. When $V_I < \phi$ the univalent adsorbate atom will acquire a positive charge number between 1 and 2. These values of the charge will approach 1 and 2 for the univalent and divalent adsorbates respectively only if an insignificant portion of the adsorbate band dips below the Fermi level. Similar considerations apply in the case of complete neutralization of divalent adsorbates, although of course, V_I is now greater than ϕ and only an insignificant portion of the E vs $|\psi|^2$ curve can remain above the Fermi level. If the valence level of the adsorbate atom falls below the bottom of the conduction band, it will remain discrete

when the atom is adsorbed. It may be possible, however, for the atom to acquire a supernumerary electron of which the energy level may be high enough to be broadened by the adjacent metal. Such adsorption will result in formation of a dipole layer with negative end outwards and the extent of the charge will depend once more on the degree of broadening, and the relative positions of the new energy level and the Fermi level.

Critique. - Gurney's work function theory was a valuable contribution to the understanding of the quantum mechanical nature of adsorbed particles. J. A. Becker had argued that cesium was adsorbed on tungsten as separate ions and neutral atoms because ions are obtained when cesium is evaporated from dilute layers of cesium on tungsten. Gurney's theory, however, explained how the adsorbate-bond could also be polar as in the case of polar molecules. In Gurney's view the charge number of the adsorbed particle would continuously vary between 0 and 1 as the work function of the composite cesium-tungsten surface changed.

Although Gurney has given a satisfactory qualitative description of how electropositive elements may result in a lowering of work function of metals, no quantitative estimates were made to check with experiment. Moreover, no mention is made of the fact that the center of the broadened adsorbate band will move up or down as the adsorbate atom moves in close to the metal and may not coincide with the original sharp ionization level of the adsorbate atom when it is at its equilibrium position.

19 - THEORY OF ATOM-METAL INTERACTIONS I ALKALI METAL ADSORPTION

Surface Sci., 6, 133 (1957)

By J. W. Gadzuk

Review. - Gadzuk has developed a 1st order perturbation technique using zero order wave functions for treating interactions between a metal substrate and alkali metal adsorbate atoms. Interaction results in a broadening and shifting of the valence level of the alkali atom with respect to the metal Fermi level. The shift is ≈ 0.3 eV upwards while the width of the broadened adsorbate valence level is $\lesssim 1$ eV.

The Shrödinger equation for describing the above interaction is

$$H_{\text{tot}} = H_m + H_a + H_{\text{int}} \quad (1)$$

in which H_m describes the unperturbed metal, H_a the unperturbed atom, and H_{int} the complete coupling with the metal. A free electron model for the metal is assumed and hydrogen-like wave functions $\psi_{n,s}$ are used to describe the adsorbate atom valence electron. The Hamiltonian in Equation (1) may be reduced to an effective one electron Hamiltonian of the form:

$$H = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4r_{\text{em}}} + \frac{e^2}{r_{\text{ei}}} - \frac{e^2}{r_{\text{ep}}} \quad (2)$$

where the last three terms represent the potential of the electron separated by a distance r_{em} from the metal, r_{ei} from the image of the positive ion and by a distance r_{ep} from the adsorbate ion. The first term is the image potential of the electron in the presence of the metal, the second is the repulsion between the electron and the image of the positive ion in the metal while the third is due to the attraction between the electron and the positive ion. Gadzuk then decomposes the Hamiltonian in two ways; in the first, the two equations

$$H_a = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_{ep}}$$

and

$$H'_{a-m} = \frac{-e^2}{4r_{em}} + \frac{e^2}{r_{ei}}$$

describe an alkali metal electron existing as a solution of H_a that is perturbed by the metal through the perturbation H'_{a-m} while the second set of equations

$$H_m = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4r_{em}} + \frac{e^2}{r_{ei}}$$

$$- H'_{m-a} = \frac{e^2}{r_{ep}}$$

describe an electron moving in a metal which has been perturbed by the presence of the alkali ion core. The technique of resolving the full Hamiltonian into an soluble part and a perturbation is only satisfactory provided that the natural width of the virtual state is less than the width of the conduction band.

The first order energy shift of the valence level is :

$$\Delta E = \frac{\langle \psi_{n,s} | H'_{a-m} | \psi_{n,s} \rangle}{\langle \psi_{n,s} | \psi_{n,s} \rangle}$$

while the broadening of the alkali atom valence level is obtained from a first order version of the Golden rule :

$$\Delta(s) \sim \sum_k \frac{2\pi}{\hbar} \rho_k |T_{i,f}|^2$$

where s is the distance of the adsorbate from the metal surface and ρ_k is the density of states in the metal which is summed over all degeneracies of the metal state. The transition matrix element $|T_{i,f}|$ is obtained from

$$T_{i,f} \sim \langle \psi_{n,s} | H'_{m-a} | u_i \rangle$$

where u_i is the single free-electron eigenfunction and $H'_{m-a} = e^2/r_{ep}$.

The centroid of the electron charge distribution may be expressed as

$$\langle z_e \rangle = \frac{1}{n_o + 1} \sum_{k=0}^{n_o+1} \int_{-L}^{+\infty} \psi_{mk}^* z \psi_{mk} dr$$

where n_o is the number of electrons in the metal ψ_{mk} is a metal wave function length of the finite cubic metal crystal and z is a length perpendicular to the metal. The centroid of positive charge is given by

$$\langle z_p \rangle = \frac{1}{en_o} \sum_{i=1}^n \rho_i(z) z_i + r$$

where ρ_i is the charge distribution of ion cores within the metal and z_i is their position. The net effect is equivalent to a single electron at $\langle z_e \rangle$ and a single positive charge at $\langle z_p \rangle$ so that a dipole moment $M_o = e(\langle z_p - z_e \rangle)$ results, since $\langle z_p \rangle \neq \langle z_e \rangle$. Gadzuk also includes an expression for M_o which is dependent on temperature. The effect of increasing T is to populate adsorbate levels and hence to decrease M_o .

Critique. - This approach by Gadzuk to the problem of the calculation of shift and broadening of an atomic level of an alkali metal atom due to interaction with a metal substrate is similar to that adopted by Bennett and Falicor in the following paper. These authors used the Hartree approximation and took care of electron spin by assuming that no more than one electron can occupy the s state of the adsorbate atom while Gadzuk used the Hartree-Fock approximation. The single electron Hamiltonian used was similar in both papers. In order to calculate broadening, Gadzuk used the Golden Rule of time dependent perturbation theory. This yields an expression involving the transition matrix element $|T_{i,f}|^2$ which is equal to $|\langle \psi_{n,s} | H'_{m-a} | \chi \rangle|^2$ with H'_{m-a} being a perturbation operator.

According to Gadzuk H'_{m-a} is just the Coulomb interaction $-e^2/r_{ep}$. It is surprising that Gadzuk used this term as the perturbation operator. A more understandable choice would have been the perturbation which couples the initial and final states : $-q^2/4r_{em} + q^2/r_{ei}$. Bennett and Falicov assumed a Gaussian distribution for the broadened adsorbate level and showed through use of Fano's theory for the mixing of a discrete atomic level with a continuum due to configuration interaction, that broadening Δ is given by $\Delta = \pi(V_E)^2 = \pi \int |\langle \chi(E, 0, \mu) | H | \phi \rangle|^2 N_O(\mu E) dE$ where H is the complete single electron operator. The squared term here is similar to $|T_{i,f}|^2$ employed by Gadzuk, the major difference being in the type of operator used. The broadening calculated from Gadzuk's approach was ≈ 1 eV which is somewhat larger than Rasor and Warners' value¹. Bennett and Falicov calculated a value of $\Delta \sim 2 - 3$ eV which is more in accord with the view of Gomer² who by consideration of a one-dimensional barrier between adsorbate atom and metal for the K - W system, showed that the potential energy barrier dropped below the Fermi level of the metal for small separations of the alkali atom from the metal surface.

Gadzuk predicts that increase in temperature effects a "thermal depolarization" of the substrate-adsorbate bond moment; that is to say a decrease of work function change should accompany increase in temperature. A similar prediction was made by Rasor and Warner.¹ Work on the adsorption of cesium on tungsten and molybdenum, indicate, however,³ that increase in temperature is accompanied by increase in work function change. Similar results were also reported by Bosworth⁴ for Na on W using contact potential techniques.

- ¹ N. D. Rasor and C. Warner, J. Appl. Phys., 35, 2589 (1964)
- ² R. Gomer and L. D. Schmidt, J. Chem. Phys., 45, 1605 (1965).
- ³ L. W. Swanson, et al., Final Report, NASA Contract No. NAS3-2596, Field Emission Corporation (1964).
L. W. Swanson et al., Final Report NASA Contract No. NASw-1082, Field Emission Corporation (1966).
- ⁴ R. C. Bosworth, Proc. Roy. Soc. A162, 32 (1937).

20 - THEORY OF THE ELECTRONIC CONFIGURATION OF A METALLIC SURFACE - ADSORBATE SYSTEM

Phys. Rev. 151, 512 (1966)

By A. J. Bennett and L. M. Falicov

Review. - When alkali metals are adsorbed on metal substrates , the sharp valence level of the adsorbate broadens (width Δ) and undergoes a shift in position, so that the adsorbate atom acquires a positive charge q of value up to $|e|$ depending on the position of the shifted maximum E_u of the valence level with respect to the Fermi level of the substrate. Bennett and Falicov have made self-consistent calculations of the quantities q , E_u and Δ as a function of electric field F and adsorbate-substrate separation z for the alkali metals K, Rb and Cs adsorbed on tungsten. The charge around the adsorbate atom was considered to be made up from the contributions of an infinitely large number of states, each contributing an infinitesimal amount of charge. The Hartree approximation was used, since this is applicable if localized states are absent. In this case, the total wave function of the system $\bar{\Psi}$ can be expressed as the simple product of one-electron wave functions

$$\bar{\Psi} = \prod_i \psi(E_{Hi}, l_i, \nu_i; \underline{r}_i)$$

where each one-electron wave function is determined by three quantum numbers: E_H , one-electron Hartree energy; l , angular momentum in a direction perpendicular to the surface; ν a third quantum number which completes identification of the state. Each of the functions ψ satisfies the Schrödinger equation:

$$H \psi = E_H \psi \quad (1)$$

where H is the self-consistent one-electron Hartree Hamiltonian obtained by minimizing the total energy E_t with respect to $\bar{\Psi}$ where

$$E_t = \langle \bar{\Psi} | H | \bar{\Psi} \rangle / \langle \bar{\Psi} | \bar{\Psi} \rangle$$

The effective charge in a volume V around the adsorbate atom is given by :

$$q = |e| [1 - q^-] = |e| \left[1 - \int_{-\infty}^{E_F} p(E) dE \right] \text{ as } T \rightarrow 0$$

The quantity E_F is the Fermi energy and $p(E)$ is the effective electronic charge per/unit Hartree of energy. It was assumed that $p(E)$ can be represented by a Lorentzian distribution

$$p(E) = \frac{1}{\pi} \frac{\Delta}{(E - E_u)^2 + \Delta^2} \quad (2)$$

where Δ is the width of the broadened level from which

$$q^- = \frac{1}{\pi} \left[\tan^{-1} \frac{E_F - E_u}{\Delta} + \frac{\pi}{2} \right] \quad (3)$$

It is assumed that $E_u - V_B \gg \Delta$. In order to justify the above expression for $p(E)$ and calculate E_u it is necessary to obtain an expression for H . This is of the form

$$H = T + V_m + V_a + V_f + V_{ee}$$

where T is the kinetic energy operator, V_m is the potential due to metal ions, V_a is the potential of the adsorbate ion, V_f is the potential due to an external electric field F , and V_{ee} is the self-consistent potential acting on one electron. Equation (1) may now be solved if H is simplified by assuming that the potential inside the metal is constant and that V_{ee} outside the metal may be replaced by a classical image potential V_{im} . In solving Equation (1), use was made of a perturbation theory approach developed by Fano, who developed the technique for studying the mixing of a discrete atomic state with a continuum due to configuration interaction. In the present problem, the metal provides the continuum of levels while the adsorbate supplies the single discrete state. This yielded:

$$p(E) = \frac{|V_E|^2}{[E - E_u]^2 + \pi V_E^2}, \text{ so that } \Delta = \pi |V_E|^2 \text{ (See Equation (2))},$$

$$\text{where } |V_E|^2 = \int |\langle \chi(E, 0, \mu) | H | u \rangle|^2 N_0(\mu E) d\mu \quad (4)$$

The function $\chi(E, i, \mu)$ is one of a continuum of metallic wave functions and the quantum numbers l and μ are the axial angular momentum and the radial linear momentum respectively. The function $N_l(\mu E)$ is the density of metallic states with angular momentum l per unit radial momentum in the plane perpendicular to the metal surface and per unit energy. The quantity E_u was obtained from

$$E_u = \langle u | H | u \rangle$$

where u is an s-like function which satisfies the Schrödinger equation

$$H_A u = (T + V_A') u = E_A' u$$

where V_A' is the potential due to the adsorbate ion modified by the effective charge q^- of the electrons in its neighborhood. After evaluating E_A by means of procedures suggested by Slater² and considering only those separations d which result in less than 10% of the charge associated with $|u|^2$ being in the metal, E_u was expressed as

$$E_u = -R_d \left[\frac{Z - S_Z - \alpha q^-}{n^*} \right]^2 - |e| Fd + \frac{(1 - \beta q^-) e^2}{2z} \quad (5)$$

where R_d is the Rydberg constant, Z is the nuclear charge of the adsorbate, n^* is the effective quantum number, S_Z is an effective shielding constant, while α and β are correlation dependent terms and n^* is an effective quantum number.

A table of values of Δ for various values of z was presented by the authors for the alkali metals K, Rb, Cs for $E = E_u$. Typical widths of 1.5 - 3.0 Å arise for d values of approximately 3 Å, although the values of Δ are stated to be unreliable at $z = 2.85$ Å since the 10% of charge

approximation mentioned above no longer holds. At this point the self-consistent solution to the problem was obtained graphically as follows: an appropriate value of Δ calculated from Equation (4) was inserted in Equation (3) and q^- was plotted as a function of E_u . On the same graph, E_u , calculated from Equation (5), was plotted against q^- for various values of F . Intersection of these two sets of curves yielded self-consistent values of E_u and q^- which were tabulated for $E = E_u = E_F = -V_I = -4.5$ eV. The results may be summarized as follows: at $z = 8 \text{ \AA}$, the three alkali metals are either neutral or ionic depending on the value of F . At $z = 2.85 \text{ \AA}$, K exhibits a true metallic character for all values of F . Although F has been treated here as though it were an externally applied field, it may in fact arise from the dipole moment caused by all other adsorbed atoms.

Critique. - Bennett and Falicov have calculated the degree of charge residing on an alkali metal atom so that dipole moments and hence work function change may be calculated for these adsorbates adsorbed on tungsten. A useful feature of the theory is that dipole moments may also be obtained as a function of coverage and the results are in reasonable agreement with the experimental results of Gomer and Schmidt.³ No account was taken of the effect of temperature on work function change.

¹V. Fano, Phys. Rev. 124, 1866 (1961).

²J. C. Slater, Phys. Rev. 36, 57 (1930).

³R. Gomer and L. D. Schmidt, J. Phys. Chem. 45, 1605 (1966).

POTENTIAL ENERGY CALCULATIONS

21 - DISCRETENESS OF CHARGE ADSORPTION MICROPOTENTIALS II - SINGLE IMAGING

J. Chem. Phys./43, 2575 (1965)

By C. A. Barlow, Jr. and J. R. Macdonald

Review. - In their paper concerning single imaging of regular arrays of nonpolarizable ions, Barlow and Macdonald consider two problems, the first of which is the calculation (neglecting boundary effects) of the field and potential outside a complete array of ions; this is useful for calculating work function changes. The second, a micropotential problem, concerns calculation of field and potential along a line perpendicular to the array through the center of a single vacancy. Ion desorption energies may be predicted from the micropotential results. Polarization effects are accounted for by incorporating a dielectric term ϵ while possible thermal disturbances to the regularity of the adion array are neglected.

Barlow and Macdonald have carefully distinguished between a number of similar though not identical potentials that have been used in the past or which are pertinent for the calculation of work function change and the ion array penetration coefficient f . Thus we have the following local potentials:

V_{aic}	Potential arising from complete adion-image array
V_e	Potential contribution from excess charge $q + q_a$ on the electrode
V_{ic}	$V_e + V_{aic}$
V_a	Potential analogous to V_{aic} but pertaining to a lattice with a single vacancy
V	$V_a + V_e$
V_{iz}	Potential due the image of a charge at 0, 0, Z

V_i	A hybrid potential $V + V_{iz}$
$V_1 = V(1) - V(Z)$	The conventional micropotential
$V_{i1} = V_i(1) - V_i(Z)$	The correct micropotential
$V_2 = V(1) - V(\infty)$	Near-field micropotentials. The enclosed brackets refer to the value of the coordinate Z.
$V_{i2} = V_i(1) - V_i(\infty)$	
$V_{ai} = V_a + V_{iz}$	where V_{i1} is a special case of V_{iz} , calculated for the image at 0, 0, -1.
$V_{ail} = V_a + V_{il}$	

The ion vacancy is situated at the point 0, 0, 1 where the cartesian coordinates X, Y, Z are expressed in terms of r , ie., $X = x/r$, $Y = y/r$, $Z = z/r$, where r is the distance of the charge centroid of the adion array from the image plane. X and Y are measured in the adsorbent plane while Z is measured perpendicular to it.

$V_a(Z)$ (and hence V_{aic}) is expressed as an infinite series which, because of its slowly converging nature, must be transformed into a more rapidly converging one in order to facilitate computation. The result consists of a closed form part and a series part which can frequently be neglected especially when $d_1 \rightarrow 0$ (Z fixed) or $Z \rightarrow \infty$ (d_1 fixed). Note that d_1 is the nearest neighbor distance in the array and $R_1 = d_1/r$. For $d_1/r \rightarrow \infty$ (Z fixed), however, the series part is dominant and calculation lengthy. Values of V_{aic}/V_∞ have been calculated as a function of Z/R_1 and are plotted in Barlow and Macdonald's paper for various positions in the lattice together with a plot of V_a/V_∞ vs Z/R_1 for one position in the lattice. Also given are plots of V_{aic}/V_∞ vs R_1 for various values of Z. The plots of potential vs Z/R_1 show that the potential curves are nearly linear between $Z = 0$ and $Z = 1$ and that the potential rise which takes place as Z/R_1 increases is essentially complete when $Z/R_1 = 1$. The use of Z/R_1 instead of Z removes much of the dependence of curve shape on R_1 .

If rearrangement possibilities on adsorption or desorption are excluded, then f is properly calculated from V_{∞} and V_{i2} , instead of from V_{∞} and V_2 because only V_{i2} includes the contribution to the adsorption energy of the adsorbing ions own image. In this case, f is given by:

$$f_2 = - \frac{V_{i2}}{V_{\infty}} = 1 - \left[\frac{V_{ai(1)}}{V_{\infty}} \right] \quad (1)$$

The rearrangement contribution to the energy of adsorption is derived from V_{ail} ; thus, the total system energy E_t is given as:

$$E_t = \left(\frac{ne}{2} \right) V_{ail} (1) N \quad (2)$$

for unit area and N particles adsorbed. n is valence of adions. The total system energy change, including rearrangement, when one adion is desorbed is:

$$\begin{aligned} \Delta E_t &= E_t(N+1) - E_t(N) \\ &= \frac{ne}{2} \left[\Delta N V_{ail}(1) + N \Delta V_{ail}(1) \right] \\ &= \frac{ne}{2} \left[V_{ail}(1) + N \Delta V_a(1) \right] \\ &= \frac{ne}{2} V_{ail}(1) (1 + \eta \tau) \end{aligned}$$

where $\Delta V_a(1)/V_a(1) = \eta$, $\Delta N/N = \eta/N$ and $V_a(1)/V_{ail}(1) \equiv \tau$. The rearrangement work is $E_r = \Delta E_t - ne \left[V_a(1) + (1/2) V_{ail}(1) \right]$ where the negative term is the energy of adsorption in the absence of rearrangement. The last expression simplifies to give

$$E_r = \left(\frac{ne}{2} \right) (\eta - 1) V_a(1) \quad (3)$$

Barlow and Macdonald conclude that the rearrangement work E_r is significant and cannot be neglected for coverages in the range of experimental interest.

Critique. - Barlow and Macdonald have made accurate and comprehensive calculations of the potential anywhere in front of a hexagonal array of nonpolarizable ions and along a perpendicular line through the center of a single vacancy in this array by transforming the slowly converging series which appears in the expressions for these potentials into a more rapidly converging one.

They have also obtained an expression for the rearrangement work which takes place on adsorption and show that it cannot be neglected in considering estimates of the ion array penetration coefficient.

Employed in these authors' theories of work function change¹ and ion adsorption energies,² the above results enable accurate and rigorous calculations to be made based on the classical model of adsorption of discrete elements into positions in a fixed array.

This model suffers from the limitations outlined by Barlow and Macdonald and which are discussed in earlier critiques in this series on Barlow and Macdonalds' classical approach.

¹ J. Ross Macdonald and C. A. Barlow, J. Chem. Phys. 44, 202 (1966) Paper 16, this review series.

² J. Ross Macdonald and C. A. Barlow, J. Chem. Phys. 39, 412 (1963) Paper 15, this review series.

SUMMARY

The first five papers in the section dealing with atom and ion desorption energies contain a priori quantum-mechanical discussions of adsorption systems. Grimley and Sutula have used a simple one-dimensional chain of atoms for the model of the adsorbent and were able to bring out some of the qualitative features of chemisorption. Thus Grimley was able to account qualitatively for the decline in heats of adsorption with coverage and also to distinguish between the different bond types: metallic, covalent and ionic. An interesting feature of mutual interactions between adsorbed atoms emerged from Grimley's treatment: appreciable interaction takes place at distances at which no significant interaction would occur in the absence of the metal substrate. The wavefunctions of the adsorbed atoms die away much more slowly with distance in the metal than do the wave functions for isolated atoms, consequently the wave functions of adsorbed atoms overlap to a greater extent at a given separation than do those for two isolated atoms at the same separation. Hemptinne's second order perturbation approach also led to a distinction between different bonding types. Unlike the above authors Ashevov was able to estimate the decrease in heats of adsorption for the coverage range $0 < \theta < 1$ for covalent adsorption and found this to be ~ 1 eV, which is in approximate agreement with experiment. Gundry and Tompkins reviewed the theory of no-bond resonance as applied to adsorption and concluded that it was not valid for the treatment of chemisorption situations and that its applicability to physical adsorption situations was doubtful.

The paper I of Higuchi, Ree and Eyring contains a classical electrostatic treatment of the heats of ionic desorption in which cognizance of the discrete nature of the adsorbate ion has been made only indirectly. A semi-empirical factor $\sqrt{\sim 0.25}$ was employed to account for repulsive forces experienced by an ion as it is displaced from the adsorbate plane. Good agreement with experiment was obtained for the system Cs/W.

In paper II, these authors developed a simple quantum mechanical method for calculating heats of adsorption for covalent and polar bonding. For covalent or slightly polar bonding, they predicted that the change in heat of adsorption due to adsorption would be equal to the change in work function.

Gadzuk and Carabateas constructed a model for relating the change in ion desorption energy (as a function of surface coverage) to the change in work function through the ion array penetration parameter f . Barlow and Macdonald have developed a more generalized model for f and show how the effects of including adion polarizability and rearrangement work modify f . Their model is, however, a semi-empirical one in so far as they include E_{ni} , the surface normal field as an adjustable parameter; moreover the authors offer no clue as to how n_e , the average charge on an adion, and how the polarizability of an adion varies with coverage. Although less accurate and less rigorous than the model of Barlow and Macdonald, the model of Gadzuk and Carabateas does enable the effect of temperature to be calculated.

The most useful paper in this series from the experimentalist's point of view for predicting heats of adsorption of a wide variety of adsorbates on different substrates is the paper of Gyftopoulos and Levine who have used a chemical approach which appears justified in view of the difficulty in making accurate and reliable a priori calculations of adsorption energies.

Although the papers of Prosen and Sachs and of Lennard-Jones were developed to explain heats of physical adsorption, in recent times such theories have enjoyed a wider utility and have been used to calculate¹ activation heats of diffusion and to explain the variation with crystal plane of the heats of binding of adsorbates such as Ba^{2+} on W.

None of the work function theories outlined below is satisfactory for the complete coverage range from 0 to 1. Except for the theories of Gyftopoulos and Levine and of Barlow and Macdonald, they are only applicable

to electropositive adsorbates adsorbed on metals. Langmuir's theory, which is dependent on knowledge of atom desorption rates, is only satisfactory up to $\theta \sim 0.5$. Rasor and Warner's theory is believed to be inapplicable because of the unlikelihood of $\Delta \ll kT$. The theory of Barlow and Macdonald, is unsatisfactory because it contains an adjustable parameter E_{ni} , the so-called surface normal field; it offers no clue as to how n_e , the charge on the adsorbed species and α , the adsorbate polarizability change with coverage. Moreover, an additional problem arises in the case of electropositive adsorbates adsorbed at high coverages: the individual adsorbed particles coalesce into a two-dimensional macrocrystal in which the adsorbate valence electrons occupy positions within a new adsorbate valence band, consequently the concept of individual discrete adsorbate elements is no longer satisfactory.

Gyftopoulos and Levine have attempted to develop a theory of work function change using a phenomenological approach which appears to have been successful for dealing with adsorption energies. The work function theory is based on a division of the work function barrier into an electronegativity barrier and into a dipole barrier. It predicts the shape of the work function curve and its magnitude only if the value of $\Delta\phi$ is known at $\theta = 1$.

Gurney first pointed out the fact that adsorption bonds could be polar in character as well as either ionic or covalent. He showed that the valence level of an adsorbed atom would broaden as the atom approached a metal, provided $V_I \sim \phi$, and that the charge on the adsorbate atom would depend on the relative positions of the adsorbate level and Fermi levels. Later authors including Rasor and Warner, Gadzuk and Bennett and Falicov also calculated the adsorbate level broadening; the latter two groups of authors calculated the shift of the valence level in addition. From the shift and broadening Δ it is possible to calculate the extent of charge residing on the adsorbate atom and if the distance between the center of the adsorbate ion and its image is known, the work function change due to adsorption can be

calculated. The paper of Bennett and Falicov predicted a larger value of Δ than that of Gadzuk (2-3 eV as opposed to ~ 1 eV); the paper also contained provision for the effect of field on n_e so that $\Delta\phi$ could be calculated as a function of coverage. At high coverages the same defect is present in this theory as in that of previous authors: an omission of the effect of lateral overlap of wave functions between neighboring ad-particles.

The main obstacle to the development of a satisfactory theory of work function change or of adsorption energies is the complexity of adsorption phenomenon. Electronegative adsorbates may adsorb in a multiplicity of binding states, each characterized by a separate dipole moment and binding energy; they may also dissociate on adsorption. There is ample evidence now that both electronegative and electropositive adsorbates adsorb on different planes of the same adsorbent with different dipole moments and binding energies, although the variation appears to be less marked with the electropositive adsorbates. The relative size of adsorbate to substrate atom, the structure of a plane--whether open or close packed--and the plane work function appear to be the relevant factors which account for the variation in adsorption properties from one crystal plane to another.

Recently, evidence has been obtained that the packing of adsorbate at monolayer coverage may, in some cases at least, be dictated by a tendency of the adsorbate to close pack on the substrate even though this may cause a mismatch between the lattice structure of the adsorbate and that of the underlying substrate. Thus Anderson and Danforth³ have explained their LEED data for the adsorption of thorium on the (100) plane of tungsten in terms of such a close packed adsorbate lattice. It is possible that the minimum work function observed in the alkali metal/transition metal systems coincides with the formation of an adsorbate lattice determined by the underlying substrate lattice, while at monolayer coverage, the adsorbate lattice is closer packed and out of registry with the substrate lattice. Tucker⁴ and more recently Bauer⁵ have also interpreted LEED adsorption

experiments performed with electronegative adsorbates in terms of the formation of chemisorbed coincidence lattices in which monolayer adsorbate lattice structures are more closely packed than is allowed by match with the underlying substrate lattice. Very strong short range repulsive lateral interactions are experienced by adsorbate particles as $\theta \rightarrow 1$ owing to the interpenetration of the electron clouds. However, longer range interactions also operate, thus repulsions between the adions and between the induced dipoles in adsorbate particles exist. Grimley has also shown how the wave functions of adsorbate particles may overlap at unusually large distances when the particles are adsorbed on a metal. Under certain conditions substrate atoms may interchange with overlying adsorbate atoms. This seems to occur with oxygen⁶ on the (100) plane of tungsten, for example, at high temperatures.

Future experimental work may illustrate the part played by either vacant or filled orbitals of the substrate or adsorbate. Much inorganic chemistry of the transition metals has been interpreted in terms of the availability of suitable orbitals for binding, and many of the concepts developed there may be applicable to the interpretation of adsorption data.

At low temperatures the adsorbate is expected to be localized at definite sites with a low probability of any atom moving to an adjacent site. As temperature is increased the vibration level of the adsorbate will be increased until finally the adsorbate will move across the surface as a two-dimensional gas. Moreover, at high temperatures, considerable mobility of the substrate atoms may develop.

In view of the above complexities which obtain in real adsorption situations, the small progress towards the development of a comprehensive theory of chemisorption is not surprising. None of the adsorption theories discussed seem applicable at high temperatures and only the phenomenological approach of Gyftopoulos and Levine seems appropriate at high adsorbate coverages. Future theoretical work on adsorption systems may

draw upon some of the elegant mathematical techniques developed to explain solid-state phenomenon. An alternative approach has been taken by Gyftopoulos and Steiner.⁷ They have refined the earlier work function theory of Gyftopoulos and Levine and have eliminated the earlier arbitrary polynomial which was fitted to a set of boundary conditions. The modified theory agrees very well with experimental data for several alkali metal/refractory metal systems. A later paper dealing with electronegative adsorbates is also promised.

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- ¹ H. E. Neustadter and R. J. Bacigalugi, Surface Sci, 6, 246 (1967).
 - ² L. D. Schmidt, J. Chem. Phys. 46, 3830 (1967).
 - ³ P. J. Estrup, et al., Surface Sci 4, 286 (1966).
 - ⁴ C. W. Tucker, J. Appl. Phys. 37, 3013 (1966).
 - ⁵ E. Bauer, Surface Sci. 7, 351 (1967)
 - ⁶ P. J. Estrup and J. Anderson, 27th Annual Conference on Physical Electronics, March 1967, p. 47.
 - ⁷ E. P. Gyftopoulos and D. Steiner, 27th Annual Conference on Physical Electronics, March 1967, p. 169.

PART II - SOME THEORETICAL AND EMPIRICAL CONSIDERATIONS OF ADSORPTION

INTRODUCTION

In this Section we shall develop phenomenological theories of certain aspects of surface adsorption that relate to recent studies performed in this laboratory. The first topic deals with an empirical treatment of work function change of Group I and II adsorbates. The effect of applied electric field on adsorbed layers constitutes the second topic. And finally, a discussion of the influence of substrate structure on surface diffusion and desorption is given.

The data employed in this section to test the theoretical models are primarily obtained from recent field emission studies of adsorption.

WORK FUNCTION CHANGE

A rigorous theory of work function change upon adsorption must account for the dipole moment strength of the ad-particle in terms of relevant substrate and adsorbate parameters. The fundamental physical properties of the adsorbate and substrate can be best categorized into electronic and geometric properties. For instance, local work function and site density are important substrate electronic and geometric parameters respectively. Independent variation of these, however, requires single crystal face studies on a variety of suitably chosen substrates. Similarly, important adsorbate parameters such as atomic radius, ionization potential and polarizability are interrelated and can be varied independently only by careful choice of the adsorbates.

In order to elucidate possible empirical relationships a plot of the maximum work function change versus the substrate work function ϕ_s for Cs on various substrates was made and showed that a linear relationship exists between $\Delta\phi_m$ and ϕ_s of the following form:

$$\Delta\phi_m = 1.09 (1.78 - \phi_s) \text{ (eV)}, \quad (1)$$

where $\Delta\phi_m = \phi - \phi_s$. This relationship indicates that ϕ_s is a fundamental substrate parameter governing $\Delta\phi_m$. On the other hand, the fundamental adsorbate parameter governing the value of $\Delta\phi_m$ appeared to be its ionization potential I_a as determined by noting an empirical relationship among various group IIA adsorbates on W. In this case a linear relationship was found to exist between $\Delta\phi_m$ and I_a of the form:

$$\Delta\phi_m = 0.65 (I_a - 9.04) \text{ (eV)}. \quad (2)$$

In view of Equations (1) and (2) we postulate the existence of an empirical relationship of the following form:

$$\Delta\phi_m = k_1 (k_2 I_a - \phi_s). \quad (3)$$

By categorizing adsorbates into group IA and IIA it was found that unique values of the parameters k_1 and k_2 could be determined independent of the respective adsorbate-substrate combination. The values of $\Delta\phi_m$ so calculated are compared with experimental values in Table I for a variety of group I and II adsorbates on several refractory metals. Because of the limited single crystal face values, average values of $\Delta\phi_m$ are also included. Interestingly, the values of k_2 are nearly the same for group IA and IIA adsorbates, while k_1 varies more significantly. Extending the empirical relationship for group IA adsorbates with the same values of k_1 and k_2 to a group IB adsorbate such as Cu did not yield quantitative agreement; this was also the case for the group IIB adsorbate Hg as also shown in Table I. The applicability of the indicated values of k_1 and k_2 to a variety of adsorbates, in spite of the fact that the adsorbate density σ_m varies, implies that the product $\mu\sigma_m$ is of fundamental interest, since according to the Helmholtz equation we have

$$\Delta\phi = 4\pi e z d \sigma_m, \quad (4)$$

where ze is the positive charge and d the dipole distance. From the values

TABLE I

Comparison of experimental values of $\Delta\phi_m$ with predictions of Equation (3); also, values of ez_m/r_a and z_m are given at σ_m .

Group I Adsorbates, $k_1 = 1.09$ and $k_2 = 0.46$

Substrates	Adsorbates	ϕ_s (eV)	$\Delta\phi_m$ (eV) calc	$\Delta\phi_m$ (eV) exp.	$\sigma_m \times 10^{-14}$ (atoms/cm ²)	ez_m/r_a (eV)	z_m
W	Cs	4.52	-2.96	-3.00 ¹	1.9	1.72	0.31
W(100)	Cs	4.70	-3.15	-3.10 ¹	---	1.84	0.33
W(110)	Cs	5.90	-4.49	-4.43 ¹	---	2.62	0.47
W	Rb	4.52	-2.98	---	---	1.74	0.28
W	K	4.52	-2.75	-2.74 ²	3.2	1.61	0.25
W	K	4.40	-2.62	-2.50 ²	---	1.53	0.23
W(110)	K	5.85	-4.20	-4.15 ²	---	2.45	0.37
W(112)	K	4.90	-3.17	-3.10 ²	---	1.90	0.29
W	Na	4.52	-2.36	-2.78 ³	4.1	1.37	0.17
W(110)	Li	5.20	-2.96	-3.00 ⁴	5.0	1.74	0.17
Ta	Cs	4.12	-2.55	-2.52 ⁵	---	1.49	0.27
Mo	Cs	4.20	-2.59	-2.66 ¹	---	1.55	0.28
Re	Cs	4.85	-3.35	-3.40 ¹	---	1.95	0.35
Ni	Cs	4.74	-3.51	-3.63 ¹	---	2.05	0.43
W	Cu	4.52	-1.07	-0.23 ⁶	---	---	---

TABLE I (cont'd)

Group II Adsorbates, $k_1 = 1.3$ and $k_2 = 0.50$

Substrate	Adsorbate	ϕ_s (eV)	$\Delta\phi_m$ (eV) calc	$\Delta\phi_m$ (eV) exp	$\sigma_m \times 10^{-14}$ (atoms/cm ²)	ez_m/r_a (eV)	z_m
W	Ba	4.52	-2.45	-2.42 ⁷	---	1.43	0.21
W	Sr	4.52	-2.14	-2.22 ⁸	---	1.25	0.175
W	Ca	4.52	-1.87	-1.85 ⁸	---	1.09	0.138
W	Mg	4.52	-0.89	-0.92 ⁸	---	0.52	0.054
W	Be	4.52	0.18	0.18 ⁶	---	0.105	-0.077
Mo (111)	Ba	4.15	-2.01	-1.85 ⁹	---	1.17	0.17
W	Hg	4.52	0.87	0.39 ¹⁰	---	---	---
Mo	Hg	4.20	1.28	0.42 ¹⁰	---	---	---

of σ_m listed in Table I it was established that the average lateral separation $a_m = 1/(\sigma_m)^{1/2}$ of the adatoms at σ_m increased roughly linearly with the adsorbate atomic radius r_a according to

$$a_m \approx 2.7 r_a (\text{\AA}). \quad (5)$$

If the reasonable (as shown later) assumption that $r_a = d$ is made, Equation (3) can be recast into the physically more suggestive form:

$$\frac{ez_m}{r_a} = 0.582 k_1 (k_2 I_a - \phi_s) (\text{eV}) \quad (6)$$

$$\text{or} \quad z_m = 0.0406 k_1 (\phi_s - k_2 I_a) r_a. \quad (7)$$

The important implication of Equation (6) is that the coulomb interaction at σ_m , which is proportional to the left side of Equation (6), has the indicated empirical dependence on ϕ_s and I_a for group IA and IIA adsorbates.

Using experimental values of r_a given by Slater¹¹, we have calculated according to Equation (7) the values of z_m given in column 8 of Table I for the various systems. Figure 1 shows that z_m diminishes nearly linearly with I_a for group IA adsorbates on W, becoming negative for $I_a > 6.5$ volts. The value of z_m for Cu was determined from Equation (7) using $\Delta\phi_m$ (exp), since $\Delta\phi_m$ (calc) was in wide disagreement. This provides a value of z_m for Cu which falls on the linear extrapolation from the group IA adsorbates. If the linear extrapolation shown in Figure 1 for group IA holds for other group IB adsorbates, we predict that both Au and Ag on W should exhibit a negative z_m . The z_m values for group IIA adsorbates on W exhibit a smaller diminution with I_a than that observed for the group IA adsorbates; thus, the boundary separating positive and negative values of z_m , which occurs at ~ 6.5 V for group IA, occurs at 8.2 V for group IIA adsorbates. Of the group IIB elements only Hg has been investigated and, as shown in Table I, exhibits a positive $\Delta\phi_m$ as predicted, although values of k_1 and/or k_2 apparently change as in the case of Cu, since quantitative agreement is lacking.

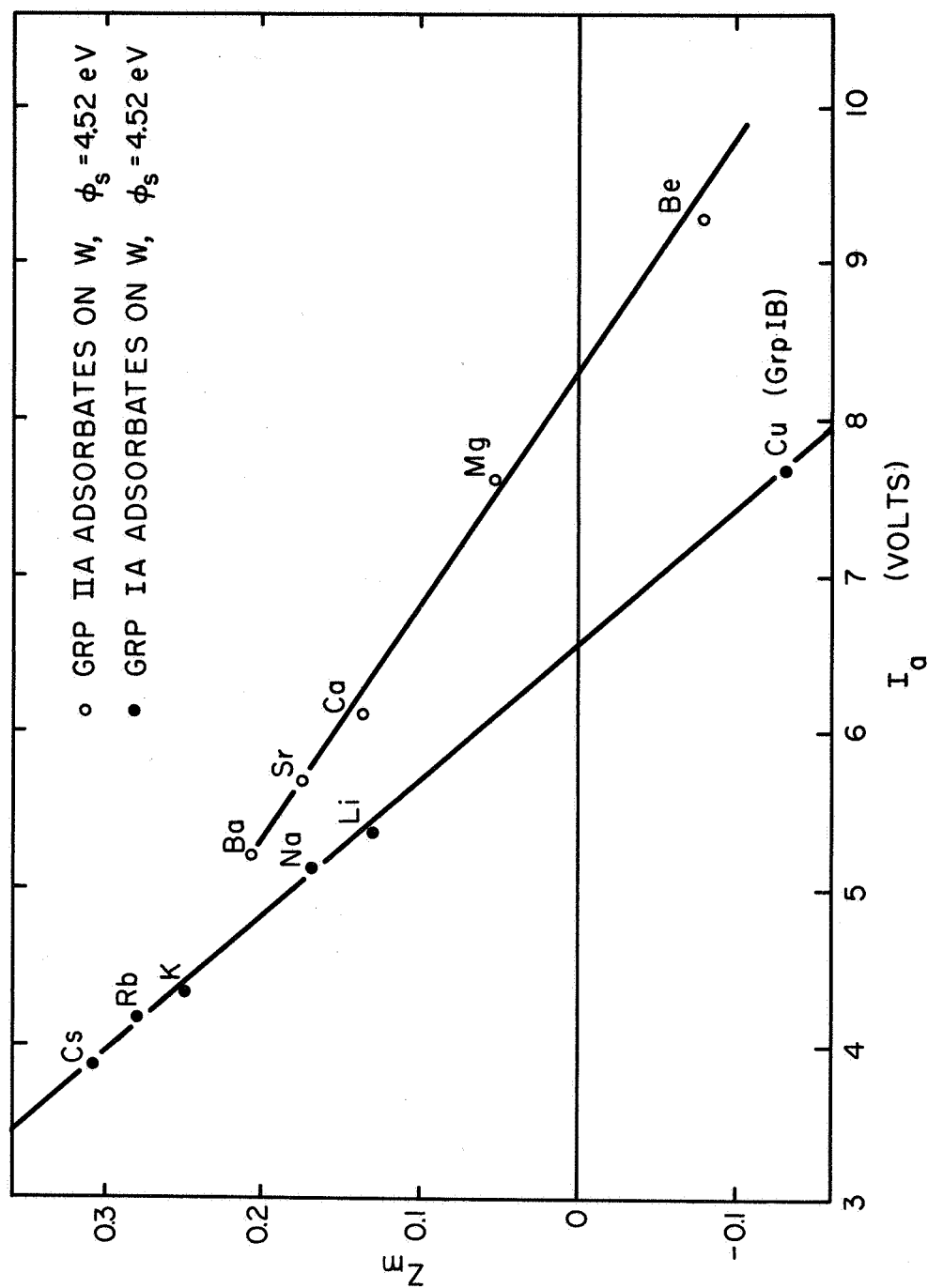


Figure 1. Plots show the variation of fractional adsorbate charge z_m at the work function minimum as a function of adsorbate ionization potential I_a . Lines interconnect the adsorbates lying within group IA and IIA of the periodic table.

The general trends for k_1 and k_2 as $\sigma \rightarrow \sigma_0$ (where σ_0 and ϕ_0 are the monolayer values) are such that $k_1 \rightarrow 1$ and k_2 remains nearly constant at 0.5; this means Equation (3) reduces to $\phi_0 \approx 0.5 I_a$ at σ_0 . Accordingly Table II shows ϕ_0 to be nearly independent of ϕ_s , except on the high work function (110) plane where it is somewhat larger. It is of further interest to note that $k_2 I_a$ is roughly equal to the average adsorbate work function. This implies that to a large degree a near monolayer of adsorbate screens out of the original double layer (or outer) contribution to the work function and the value of ϕ_0 is determined primarily by the average work function of the bulk adsorbate. These results illustrate the independence of near monolayer work function on bulk properties of the substrate and the ability of a condensed metallic monolayer to exhibit its approximate work function regardless of the underlying substrate, a point emphasized some years ago by Dobretsov¹². For this to occur exactly, the adsorbate layer must interact sufficiently to establish a quasi conduction band so that both the inner and outer contributions to the work function are established.

In order to investigate the existence of similar functional relationships as $\sigma \rightarrow 0$ the variation of μ_0 with ϕ_s and I_a would be of fundamental interest. The only extensive data of this nature is the recent field emission measurements² of μ_0 for the K/W system on various crystal faces. These results show μ_0 to increase nearly linearly with ϕ_s according to the following empirical relationship:

$$\mu_0 = 2 e z_0 d_0 = 4.1 (\phi_s - 2.0) (D) \quad (8)$$

Making the same assumption as before, i.e., $d_0 = r_a$, Equation (8) can be recast into a form similar to Equation (7), where it is found that $k_1 = 2.17$ and $k_2 = 0.46$. Assuming $r_a = 2.60 \text{ \AA}$ and using the above mentioned values of k_1 and k_2 , the values of z_0 calculated for the (110) and (100) planes of the Cs/W system are 0.93 and 0.67 respectively. These empirically calculated values of z_0 compare favorably with those calculated from the experimental values of μ_0 using $d_0 = 2.60 \text{ \AA}$ as shown in Table III. Hence, we conclude

TABLE II

Summary of work function values at its minimum $\bar{\phi}_m$ and for a saturated Cs layer $\bar{\phi}_o$.

<u>Substrate</u>	<u>$\bar{\phi}_m$ (eV)</u>	<u>$\bar{\phi}_o$ (eV)</u>
Mo	1.54 ± 0.05	1.82 ± 0.05
W	1.52 ± 0.05	1.80 ± 0.05
W (100)	1.60 ± 0.05	1.76 ± 0.05
W (110)	1.47 ± 0.05	2.18 ± 0.05
Re	1.45 ± 0.05	1.77 ± 0.05
Ni	1.37 ± 0.05	1.80 ± 0.05

TABLE III

Possible values of z_o and d_o based on experimental values of μ_o for Cs on the (110) and (100) planes of W.

Plane	$2ez_o d_o$ (D)	d_o (Å)	z_o
110	24.6	2.60	0.98
110	24.6	1.65	1.55
100	13.2	2.60	0.53
100	13.2	1.65	0.83

that the empirical relationships given in Equation (6) - (8) are also operative as $\sigma \rightarrow 0$.

The concept first put forth by Gurney¹³ and expanded by others^{12, 14-17} that the position of the exchanged broadened valence level of the adsorbate relative to the substrate Fermi level is critical in establishing the value of ze is supported by these empirical relationships. For example, the empirically established fact that z is proportional to $\phi_s - k_2 I_a$ is in accord with the qualitative expectations of the Gurney model. Further evidence supporting this model comes from the fact that the condition for neutral adsorption (i. e., $z = 0$) for group IIA adsorbates occurs at a larger value of I_a than group IA adsorbates as shown in Figure 1. According to the theoretical concept of metallic adsorption $z = 0$ occurs for group IA adsorbates when the broadened adsorbate valence band is approximately centered on the Fermi level (i. e., $I_a - \phi_s + V(x) = 0$, where $V(x)$ is the shift of the broadened valence level in the adsorbed state.) On the other hand, the broadened valence level for group IIA adsorbates must lie completely below the Fermi level for neutral adsorption; hence, the condition $I_a - \phi_s + V(x) \approx \Gamma$, where Γ is the half-width of the adsorbate level, must be met. Provided $V(x)$ does not increase significantly, this requires a larger value of I_a in agreement with the Figure 1 results.

Thus, the theoretical picture of metallic adsorption is given further experimental verification by these results, and in addition, empirical relationships for estimating the sign and magnitude of $\Delta\phi_m$ are set forth. From the experimental standpoint unequivocal means of determining dipole length would be desirable in order that ze may be determined from experimental values of μ . At the present, only educated guesses can be made by assuming ionic or atomic radii for the adatom as given in Table III. Clearly, the ionic radius is too small to give meaningful values of z for the (110) plane; hence, the value of d must lie near the atomic (or metallic) radius of Cs at least for the (110) which, in turn, seems inconsistent with $z \approx 1$ and a measured value of a much larger than that of an isolated ion. However, the

screening of the adsorbate charge constitutes $\sim 0.5 \text{ \AA}$ of d due to the finite dielectric constant of the metal; also with the present state of knowledge, one cannot predict a priori the polarizability of bonding electrons. In view of these uncertainties in d , the values of ze can only be given semiquantitatively even though experimental values of μ can be obtained. However, the trends in z with I_a and ϕ_s as discussed in this section are meaningful and provide further insight into the mechanisms of dipole moment formation for metallic adsorption systems.

THE INFLUENCE OF ELECTRIC FIELD ON ADSORPTION PHENOMENA

The effect of an external electric field on such adsorption processes as diffusion, desorption and work function change can yield potentially useful information on the ad-particle/substrate interaction. Because the static electric field strength at metal surfaces is typically 10^7 V/cm , inordinately large applied fields are required to effect the physical state of the ad-particle. The application of the field electron microscope to surface adsorption studies has led to a natural means of investigating adsorption and surface processes under high field conditions.

In this section we therefore wish to examine recent theoretical interpretations and models of the effect of electric field on work function change, adsorbate distribution, surface diffusion and desorption. The classical interaction terms between the ad-particle and applied field are: (1) a field-dipole interaction given by

$$E_{\mu} = \mu F \cos \epsilon, \quad (9)$$

where μ is the dipole moment strength, F , the applied field strength and ϵ the angle between μ and F ; (2) a polarization term of the form

$$E_a = \frac{1}{2} \alpha F^2, \quad (10)$$

where α is the adsorbate polarizability. For nonlocalized bonding, eg., metallic or ionic bonding, with which we will be primarily concerned, $\epsilon \approx 0$; however,

in the case of diatomic adsorbates or coadsorption, where substrate structure is a more important factor, ϵ may vary significantly from zero.

Effect on Work Function

The applied field alters the zero field dipole moment μ_0 as follows:

$$\mu = \mu_0 + \frac{a F}{\epsilon} \quad (11)$$

where $\epsilon = F/F_0$ is the ratio of the externally applied field to the effective field at the adsorbate. Thus the expression for the work function becomes:

$$\phi_F = \phi + \frac{g \pi a F \sigma_0 \theta}{\epsilon} \quad (12)$$

where θ is the fractional monolayer coverage and g is 2 or 4 depending upon whether the dipole moment is partly or wholly contained in the ad-particle. In field emission studies an atomistic approach to the influence of applied field on ad-particles presented by Schmidt and Gomer² simply substitutes Equation (12) into the Fowler-Nordheim expression which may be expressed in terms of the directly measurable field emission current I and applied field F as

$$I = \frac{BF^2}{\phi t^2(\phi, F)} \exp \left[- \frac{b \phi^{3/2} v(\phi, F)}{F} \right] \quad (13)$$

where $t(\phi, F)$ and $v(\phi, F)$ are tabulated¹⁸ nondimensional functions which take into account the image correction, B is proportional to emitting area, and $b = 6.8 \times 10^7$ when F is in V/cm, and ϕ in eV. It can be shown that field induced work function changes that are small compared to ϕ (i.e., $\phi > \phi_F - \phi$) are manifested in the Fowler-Nordheim equation through the pre-exponential term rather than through the exponential term. The variation of the pre-exponential term can thus be utilized as an independent method of evaluating the value of the adsorbate polarizability as a function of θ . This can readily be shown by first expanding $\phi_F^{3/2}$ as follows:

$$\phi_F^{3/2} \approx \phi^{3/2} + \frac{3 \phi^{1/2} g \pi a F \sigma_o \theta}{2\epsilon} \quad (14)$$

By noting that $v(\phi, F)$ can be approximated by¹⁹ $v(\phi, F) = 0.943 - 0.146 \times 10^{-6} F/\phi^2$ and by combining this with Equations (13) and (14) the expression for the experimental intercept $\ln A$ of a Fowler-Nordheim plot can be given by

$$\ln A = \ln \frac{B}{\phi_F t^2 (\phi_F, F)} + \frac{9.94}{\phi^{1/2}} - \frac{9.65 \times 10^7 \phi^{1/2} g \pi a \sigma_o \theta}{\epsilon} \quad (15)$$

Since for $\sigma = 0$

$$\ln A_s = \ln \frac{B}{\phi_s t^2 (\phi_s, F_s)} + \frac{9.94}{\phi_s^{1/2}} \quad (16)$$

where the subscript s refers to the clean substrate, it is possible by combining Equations (15) and (16) to obtain the following expression for a/ϵ

$$\frac{a}{\epsilon} = \frac{\log \frac{\phi_s t^2 (\phi_s, F_s)}{\phi t^2 (\phi, F)} - \log \frac{A}{A_s} + 4.33 \left(\frac{1}{\phi^{1/2}} - \frac{1}{\phi_s^{1/2}} \right)}{4.20 \times 10^7 \phi^{1/2} g \pi \sigma_o \theta} \quad (\text{cm}^3), \quad (17)$$

where ϕ_F has been replaced by its approximate value ϕ in the first term of the numerator. The values of a/ϵ for Cs on the (110) and (100) planes of W have been evaluated according to Equation (17) from experimental values of $\log A/A_s$, σ and ϕ . The value $g = 2$ was employed thereby implying an induced dipole moment centered on the plane of electric neutrality.

In order to evaluate ϵ and hence a , we assumed a Topping²⁰ array of field induced point dipoles centered on the image plane. The effective field at a specified adsorption site is therefore reduced by the accumulated effect of the field induced dipoles in the ad-layer and, for a square lattice site array, is given by

$$F_o = \frac{F}{\epsilon} = \frac{F}{1 + 9a (\sigma_o \theta)^{3/2}} \quad (18)$$

where $\epsilon = 1 + 9a (\sigma_o \theta)^{3/2}$ can be visualized as a two dimensional dielectric constant of the ad-layer.

Using the above expression for ϵ values of a were calculated as shown in column 6 of Table IV. The two main observations from these results are: (1) the values of a appear relatively constant over the range of θ and (2) the mean value of a is slightly lower for the (100) ($\bar{a}_{100} = 13 \text{ \AA}^3$), compared to that for the (110) ($a_{110} = 23 \text{ \AA}^3$). It is interesting that the value of a determined in each case is below the free atomic value, which ranges from 40 to 60 \AA^3 , and well above the value of 2.8 \AA^3 reported for the ionic state²¹. Because of the uncertain accuracy of a , particularly at lower values of θ , it is not warranted to pursue a more detailed interpretation based on the smaller variations of a with θ . The fact that values of a given in Table IV do not show any large variation at θ_m is evidence that reported² deviations of the experimental $\Delta\phi(\theta)$ data from the Topping model^{2,20} for $\theta > \theta_m$ cannot be attributed to a radical change in the effective value of a near θ_m . This lends support to the hypothesis that rearrangement of the adsorbate layer at $\theta > \theta_m$ is responsible for the departure from the Topping model assumption of a smoothly varying adsorbate interspacing with θ under conditions of mobile adsorption.

Thus, the effect of an externally applied field on the work function can be meaningfully examined and understood by field emission technique. The information concerning the ad-particle polarizability can be seen to provide important insight into its electronic environment.

Effect of Field on the Equilibrium Coverage

At temperatures sufficient to initiate surface mobility of an electro-positive adsorbate, a reversible increase or decrease in coverage may

TABLE IV

Calculation of adsorbate polarizability α for Cs on W by analysis of the Fowler-Nordheim equation pre-exponential factor according to Equation (17).

$\sigma_x 10^{14}$ (atoms/cm ²)	(100) Plane				
	θ	$\log A/A_s$	ϕ (eV)	$\frac{\alpha}{\epsilon} (\text{\AA}^3)$	$\alpha (\text{\AA}^3)$
2.50	0.89	0.65	1.65	13.5	17.5
2.40	0.86	1.07	1.63	8.9	12.7
2.30	0.82	0.89	1.61	12.1	19.4
2.20	0.79	0.83	1.67	12.0	18.5
1.85	0.66	0.94	1.84	9.2	11.7
1.22	0.44	0.81	2.22	9.3	10.5
1.08	0.39	0.36	2.61	11.7	13.4
0.90	0.32	0.34	2.87	9.7	10.4
0.74	0.26	0.34	3.13	7.0	7.3
0.32	0.11	0.08	3.93	8.4	8.5

(110) Plane					
2.62	0.94	0.42	2.13	11.6	20.7
2.56	0.91	0.73	2.03	9.9	15.5
2.48	0.89	0.63	1.91	12.9	23.6
2.35	0.84	0.72	1.76	15.2	29.9
2.22	0.79	1.03	1.65	17.0	34.5
1.70	0.61	1.34	1.54	16.0	23.6
1.64	0.59	1.34	1.57	15.7	22.3
1.40	0.50	0.97	1.79	19.3	27.2
1.20	0.43	1.01	2.09	13.4	15.9
1.03	0.37	0.46	2.42	21.0	26.2
0.85	0.30	0.28	2.85	20.5	23.9
0.60	0.21	0.35	3.46	13.4	14.2

occur in the high field region of a field emitter with increasing magnitude of positive or negative field respectively. After a period of time a new equilibrium adsorbate distribution is established, and the non-uniform coverage can be "frozen in" by rapid reduction of the emitter temperature to 77°K. The results shown in Figure 2 consist of the measurement of the Cs coverage ratio at the emitter tip σ_t to that of the shank σ_s as a function of field strength for Mo and W substrates in various coverage ranges. The coverage distribution in the high field region of the emitter tip appeared from pattern analysis to be reasonably uniform in spite of the 15% variation of field over this region and was determined by utilizing a known relationship between work function and coverage²¹. It was assumed that the coverage in the zero field region of the emitter shank was not altered by changes occurring at the emitter tip because of the large ratio of surface area of the shank to that of the tip, which is approximately 10^5 . The range of applied negative and positive fields was limited by excessive field emission and field desorption of the adsorbate respectively.

The results of the field effect on the equilibrium Cs coverage clearly indicated the process to be thermodynamically motivated and kinetically controlled by the rate of surface diffusion. The application of the field apparently alters the chemical potential of the ad-layer in the high field region, while not affecting the chemical potential in the zero field region of the emitter shank. Since thermodynamic equilibrium requires a balance of chemical potentials in both high and zero field regions of the emitter, the surface concentration of Cs rearranges until the thermodynamic imbalance is removed. These considerations can be expressed more quantitatively by postulating field interactions with the ad-layer similar to those discussed in the introduction and lead to the following relation between equilibrium coverage and field:

$$kT \ln \left[\frac{\sigma_t}{\sigma_s} \left(\frac{\sigma_o - \sigma_s}{\sigma_o - \sigma_t} \right) \right] = H(\sigma_t) - H(\sigma_s) + \frac{a}{2} F^2 - \frac{\mu F}{F} \quad (18)$$

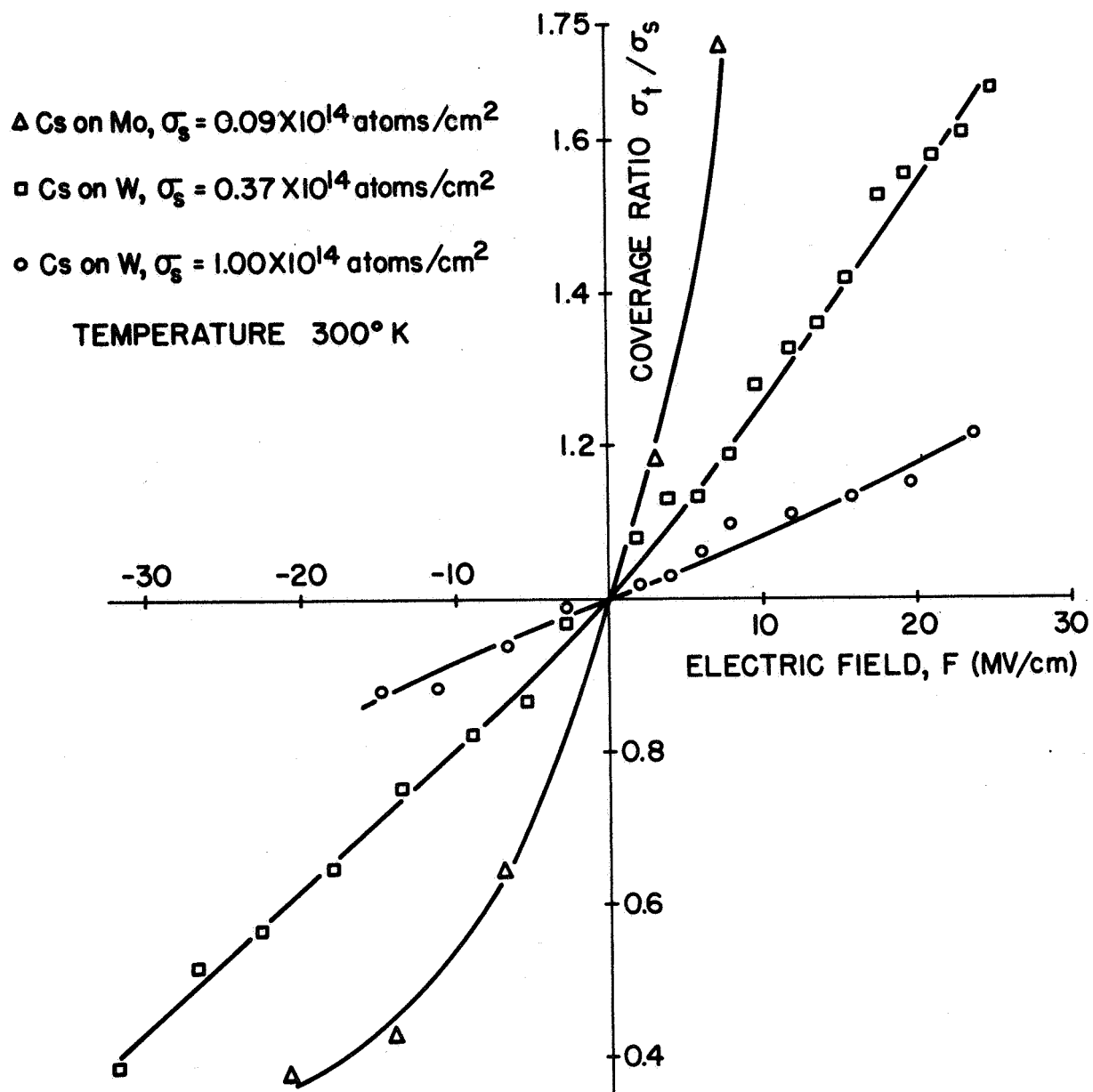


Figure 2. Variation of the ratio of cesium coverage at the emitter tip σ_t and shank σ_s with applied field F.

where $H(\sigma_t)$ and $H(\sigma_s)$ are the coverage dependent zero field heats of adsorption. Equation (18) can be further simplified by noting that over most of the field and coverage range investigated, the $\frac{a}{2} F^2$ term can be neglected when compared with other terms of Equation (18).

The validity of the above model can be tested by letting $\Delta E = H(\sigma_t) - H(\sigma_s)$ and plotting the data of Figure 2 in the form $kT \ln \frac{\sigma_t}{\sigma_s} \left[\left(\frac{\sigma_o - \sigma_s}{\sigma_o - \sigma_t} \right) \right] - \Delta E$ vs F ; the slope of the resulting straight line yields a value for μ . Figure 3 shows the data plotted in this fashion for Cs on W, for which reliable $H(\sigma)$ and $\theta(\sigma)$ data exist²²; reasonably good straight lines are obtained from which values for μ of 3.7 and 4.3×10^{-18} esu were determined at Cs coverages of 1.00 and 0.37×10^{14} atoms/cm² respectively. Throughout the field and coverage range investigated $\Delta E \gg kT \ln \frac{\sigma_t}{\sigma_s} \left[\left(\frac{\sigma_o - \sigma_s}{\sigma_o - \sigma_t} \right) \right]$ so that the values of μ hinge critically on the accuracy of $H(\sigma)$ data. Values of μ determined at these coverages by the Helmholtz equation are generally a factor of 2 greater than those determined by the field effect. Since both methods of determining μ involve averages whose weighting factors are different, the order of magnitude agreement between the μ values determined by the two methods lends support for the mechanism suggested by Equation (18).

The reason for the much smaller field effect at the higher Cs coverage as shown in Figure 2 is due to a decrease in average μ with increasing σ which stems from the larger contribution of mutual depolarization effects at higher coverage. Thus, only mobile adsorbates exhibiting large dipole moments would be expected to show an appreciable variation of the equilibrium coverage with applied field.

Effect of Field on Thermal Desorption

The effect of positive field on thermal desorption (better known as field desorption) has been investigated for a variety of systems^{23, 24} including cesium on tungsten at low coverage²⁵, and recently treated theoretically²⁶ for various types of adsorption. We have carried out such a study for Cs on W semi-quantitatively over the coverage range 0 to 1 monolayer and

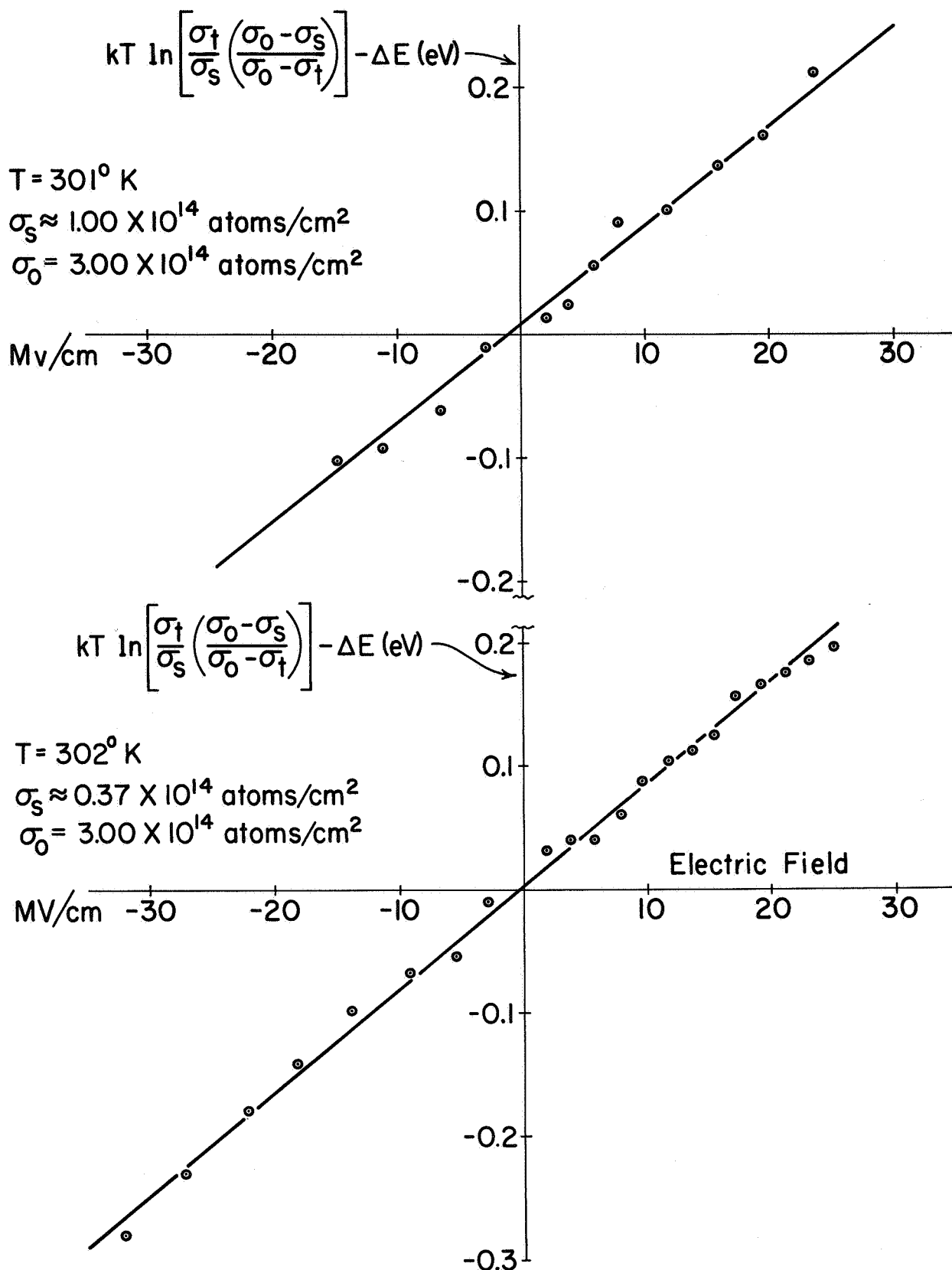


Figure 3. Data of Figure 2 plotted according to Equation (18).

quantitatively at high coverages (i. e., $\sigma = 2.9 \times 10^{14}$ atoms/cm²).

Including only the reduction of the Schottky saddle for desorption of ions and neglecting all other field interactions, it can be deduced from Figure 4 that the variation of desorption energy E_p^F of a singly charged ion e with positive field is

$$E_p^F = E_a^0 + I_a - \phi - e^{3/2} F^{1/2} \quad (19)$$

where E_a^0 is the zero field desorption energy for neutral atoms and polarization corrections are excluded. The rate constant k_p for field desorption is therefore given by

$$k_p = \nu s \exp (-E_p^F/kT),$$

where ν is the usual frequency factor and s is a complicated function involving transition probabilities and/or entropy effects.

The changes in the field emission pattern during Cs desorption from a partially covered (100) oriented tungsten emitter indicated that desorption occurred successively from planes with locally decreasing ϕ ; this means variation in ϕ from plane-to-plane override variations in E_a^0 in Equation (19) in determining the local activation energies and hence rates of field desorption.

Table V lists the fields required to initiate desorption over a range of Cs coverages. The maximum in desorption field occurs near the work function minimum ($\phi_m = 1.55$ eV at $\sigma_m = 1.90 \times 10^{14}$ atoms/cm²) in agreement with Equation (19) provided that the decrease in ϕ with σ is larger than the combined decrease in E_a^0 and other omitted terms in Equation (19). In general, the known variations of E_a^0 and ϕ with σ confirm these explanations. On the other hand, the relatively large change in desorption field between 1.20 and 1.35×10^{14} atoms/cm² cannot be explained by changes in ϕ and E_a^0 alone, but must involve significant contributions from other terms, since compensating changes in ϕ and E_a^0 occur in this

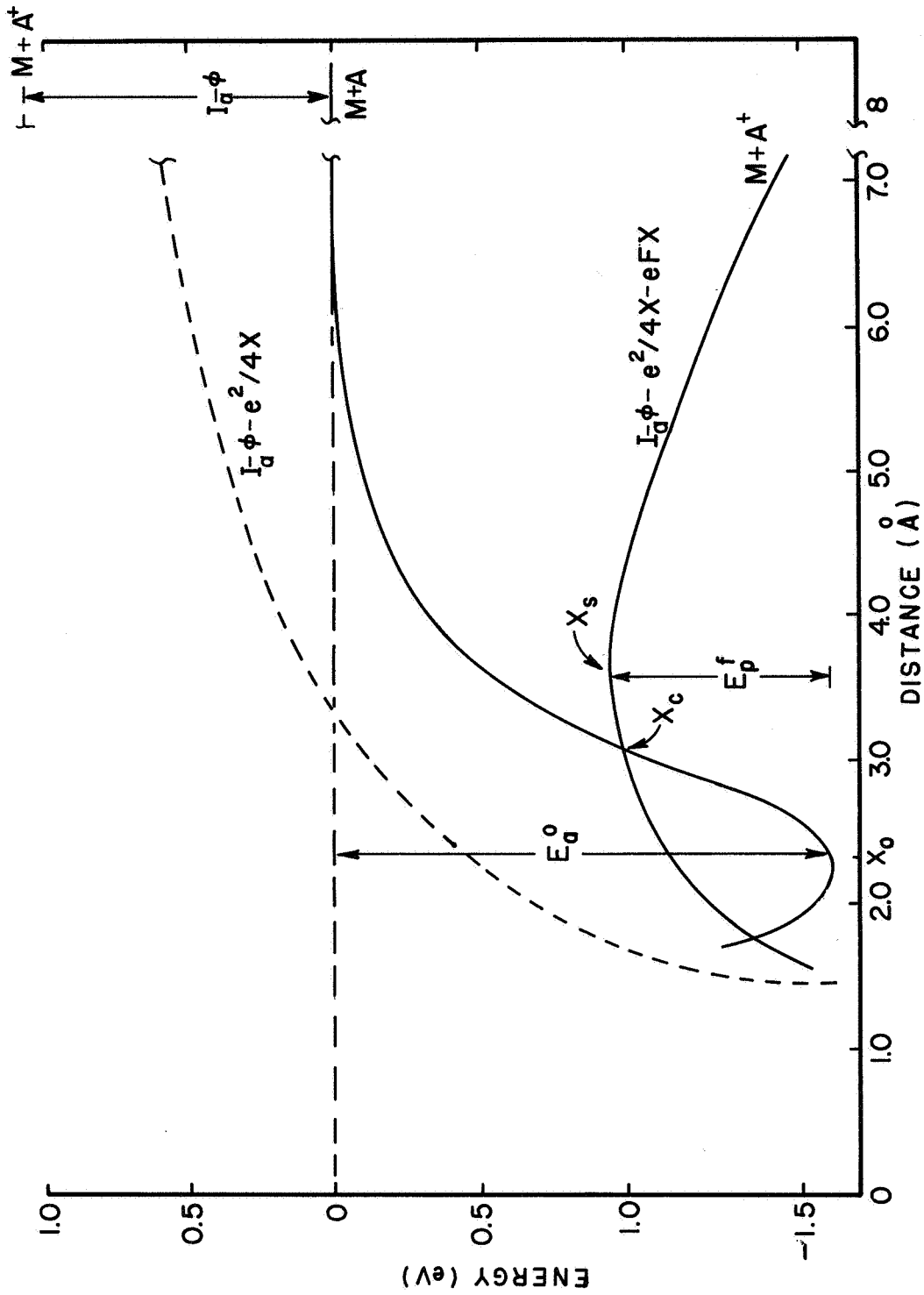


Figure 4. Potential energy diagram for quasi-metallic (i.e., non-ionic) adsorption in the presence of an applied field. The $M+A^+$ curve is an image potential (dashed line) which is altered by the field so as to form a Schottky saddle to the right of the M+A ground state curve. When $I_a - \phi$ is small or negative the ionic curve may be the ground state curve at X_0 and thus lead to ionic adsorption. No polarization effects have been included in the diagram.

TABLE V
Fields and Temperatures Required for the Onset of Field Desorption
at Various Cesium Coverages

<u>ϕ (eV)</u>	<u>$\sigma \times 10^{-14}$ (atoms/cm²)</u>	<u>F(MV/cm)</u>	<u>T(°K)</u>
1.81	3.00	59	93
1.83	1.35	62	99
2.00	1.20	40	114
2.70	0.70	42	95
4.30	0.07	39	~100

coverage range.

For Cs coverage in excess of 1.9×10^{14} atoms/cm² (the coverage corresponding to the work function minimum) the rate of field desorption decreases with decreasing coverage due primarily to the reversal in the dependence of ϕ on σ , thus making it possible to measure E_p^F as a function of F . Such measurements were carried out in the coverage and work function interval 2.9 to 2.7×10^{14} atoms/cm² and 1.81 to 1.78 eV respectively. This coverage interval brackets the atom density (2.73×10^{14} atoms/cm²) of the (100) plane of bulk cesium and, therefore, should be considered close to monolayer coverage. The field emission patterns corresponding to the initial and final coverages over which the desorption rates were measured indicated field desorption to occur primarily from the higher work function {110} regions of the emitter in accordance with Equation (19) if the anisotropies in ϕ exceed those of E_a^0 .

The results obtained are given in Table VI and show a general decrease in E_p^F with increasing F , although the trend is not monotonic. It is interesting to note that the decrease in $\log \nu$ s with increasing field, noted in previous field desorption studies involving other adsorbates^{23,24}, and also for Cs on tungsten at low coverages²⁵, was not observed in the high coverage results reported here. In order to eliminate the possibility of complicated effects on the pre-exponential factor of Equation (20) due to field desorption from a mobile layer^{23,27}, the measurements were confined to a field and temperature range such that field desorption occurred from an effectively immobile layer. It can be concluded from the normal and constant $\log \nu$ s values over the investigated field range that the transition from the ground adsorbed state to the ionic state at x_c (see Figure 4) is rapid and not altered by field.

Discussion of Results

According to the simplified model depicted in Figure 4 and the considerations leading to Equation (19), the position of the Schottky saddle is given by

TABLE VI
Variation of E_p^F and $\log \gamma$ s with F in the cesium
coverage range $\sigma = 2.9$ to 2.7×10^{14} atoms/cm²

E_p^F (eV)	$\log \gamma$ s	F (MV/cm)	T (°K)	x (Å)
0.791 \pm 0.021	12.68 \pm 0.41	---	252-276	∞
0.507 \pm 0.014	15.83 \pm 0.49	30.9	135-145	12.10
0.455 \pm 0.016	14.45 \pm 0.63	33.9	128-141	11.70
0.386 \pm 0.018	12.58 \pm 0.42	35.9	125-135	11.65
0.323 \pm 0.021	10.47 \pm 0.83	37.9	121-133	11.45
0.332 \pm 0.015	11.03 \pm 0.62	39.9	116-130	11.33
0.362 \pm 0.013	12.62 \pm 0.54	39.9	116-127	11.23
0.393 \pm 0.031	14.46 \pm 0.60	42.9	117-125	10.75
0.366 \pm 0.013	13.26 \pm 0.56	42.9	114-123	10.83
0.371 \pm 0.013	13.87 \pm 0.55	46.2	111-119	10.48
0.325 \pm 0.011	12.51 \pm 0.50	48.9	106-115	10.34
0.326 \pm 0.014	13.08 \pm 0.67	52.9	103-110	10.08
0.291 \pm 0.021	11.90 \pm 1.02	55.9	100-107	9.97
0.287 \pm 0.021	12.58 \pm 1.05	58.9	95-101	9.82

$$x_s = \frac{1}{2} \left(\frac{e}{F} \right)^{1/2} \quad (21)$$

and is approximately 2.4 \AA at the highest field investigated. Since this is less than the atomic radius of Cs, it is unlikely that the expression for x_s is valid and suggests that more detailed field interactions must be considered. Least squares analysis of the data of Table VI according to equation (19) with the inclusion of a μF and $\frac{1}{2}(a_a - a_i)F^2$ term,

$$E_p^F = E_a^o + I_a - \phi e^{3/2} F^{1/2} + |\mu| F + \frac{1}{2}(a_a - a_i) F^2, \quad (22)$$

where a_a and a_i are the polarizabilities of the atomic and ionic states, leads to values for μ , $a_a - a_i$, and $E_a^o + I_a - \phi$, which are $1.14 \times 10^{-18} \text{ esu}$, 65 \AA^3 , and 2.32 eV respectively. The resultant fit of Equation (22) to the data is shown in Figure 5; Equation (19) is also plotted showing its failure to fit the data. The calculated value for $E_a^o + I_a - \phi$ term based on the measured E_a^o and ϕ values is 2.25 eV ; the μ and a values are reasonable if a polarizable atomic (i.e., quasi-metallic) ground state²⁶ is assumed.

A more comprehensive investigation of the theory of field desorption²⁶ shows that additional F and x dependent terms should be considered; in summary they are: 1) evaluation of ϕ_c rather than ϕ_∞ ; 2) inclusion of a field-induced work function change $\Delta\phi_c^F = 4\pi\sigma a F$ evaluated at x_c ; 3) derivation of effective fields for the terms involving F ; 4) an additional term correcting for the polarization of the ad-layers by the ion formed at x_c . Inclusion of these corrections in Equation (19) leads to the following:

$$E_p^F = E_a^o + I_a - \phi_c + \Delta\phi_c^F + \mu F_o + \frac{a_a}{2} F_o^2 - \frac{a_i}{2} F_s^2 - \frac{e^2}{4x_s^3} - \frac{eFx_s}{y^2 + x_s^2} - \frac{12.5 a_a e^2 x_s^2}{(y^2 + x_s^2)^3} \quad (23)$$

where y is the lateral distance between ad-atoms and the subscripts o , c , and s refer to distances from the surface noted in Figure 4. The origin and

method of calculation of these terms are given in reference 26 where the adatom is treated as a polarizable point dipole. Equation (23) was solved for x_s (the position of the Schottky saddle) by assuming $x_c \approx x_s$ and employing the following values for the various constants: $\alpha_a = 50 \text{ \AA}^3$, $\alpha_i = 3 \text{ \AA}^3$, $\mu = 2.8 \times 10^{-18}$ esu (determined from $\mu = \Delta\phi/4\pi\sigma$), and $x_o = 2.6 \text{ \AA}$ (bulk atomic radius). The values of x_s consistent with the respective E_p^F and F are given in Figure 5 and yield x_s values considerably larger than those evaluated by Equation (22) which decrease with increasing field. Throughout the field range covered, the $\Delta\phi_c^F$ term is the predominate polarization correction due to the large value of α . Inclusion of the polarization and field-dipole interactions yields a value of $x_s = 9.8 \text{ \AA}$ at the highest field in contrast to the unlikely value of 2.4 \AA with the omission of such corrections. Thus, it appears appropriate to depict adsorbed Cs (at this coverage) in a polarizable (quasi-metallic) ground state at x_o , with a transition to an ionic state at $x > x_c$ in the presence of a field.

It should be emphasized that picturing an adsorbed metallic layer as discrete particles, so that one may speak of atomistic properties such as α and μ , is somewhat approximate. This is particularly true at lateral separations approaching bulk value so that overlap of wave functions between adatoms becomes appreciable. In such cases the field desorption mechanism must approach that of field evaporation from the bulk adsorbate.

Effect of Electric Field on Cesium Surface Diffusion

In order to illustrate the effect of field on surface diffusion let us consider the temperature dependence of the surface diffusion rates of Cs on W in the presence of an electric field varying from -22 to +13 MW/cm for two different, but successive, modes of surface diffusion with an initial Cs coverage of 0.6×10^{14} atoms/cm² (approximately 0.2 monolayer). These modes, shown in Figure 6, involve diffusion around the (110) plane along close-packed (110) type ledges of the field emitter (type A) and diffusion into the (110) plane over (110) ledges (type B). Values of the field-dependent

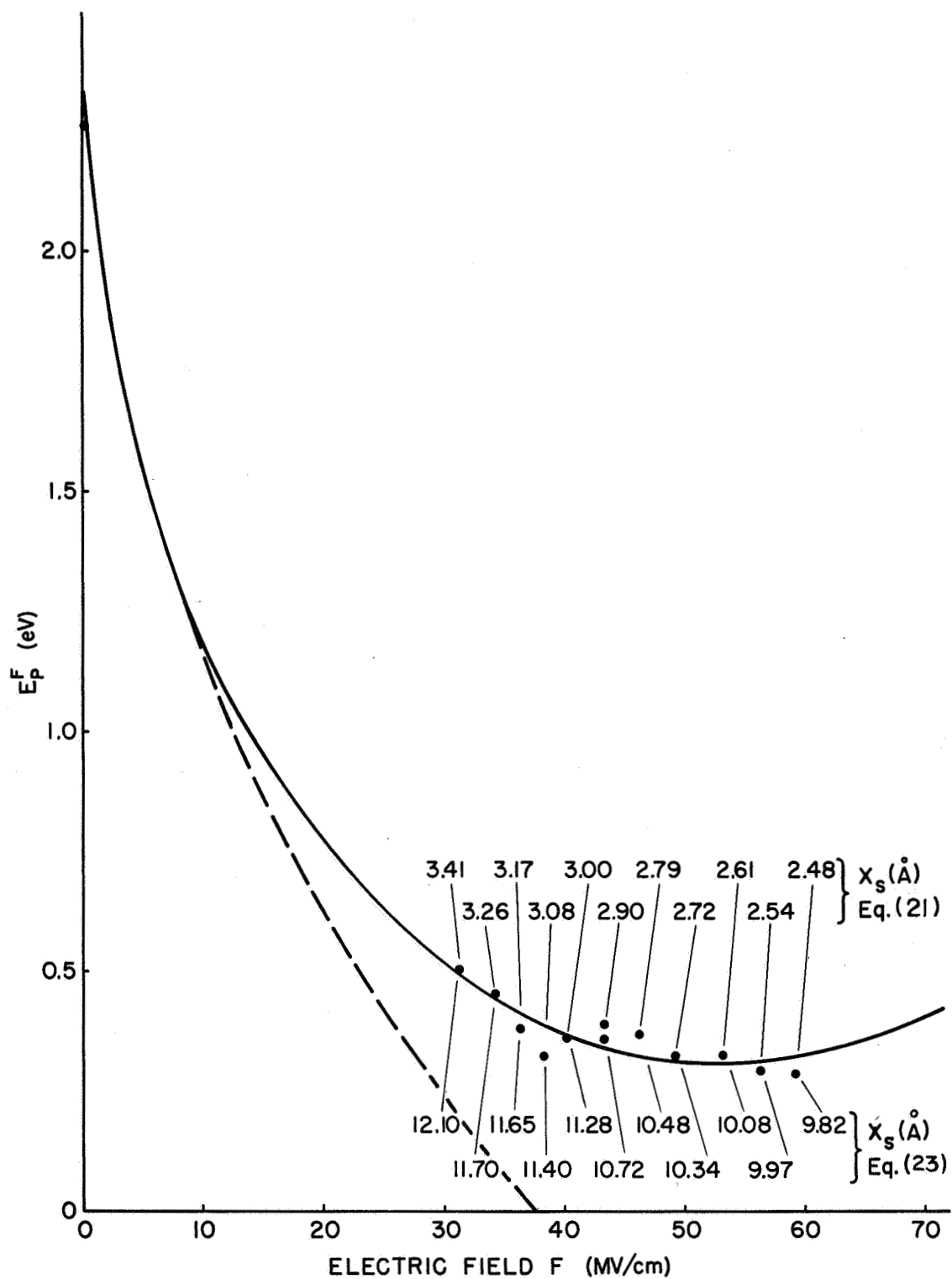


Figure 5. Least squares fit of equation (22) to data of Table VI. Dashed line shows variation of E_p^F according to equation (19). Values of x_s calculated according to equations (21) and (23).

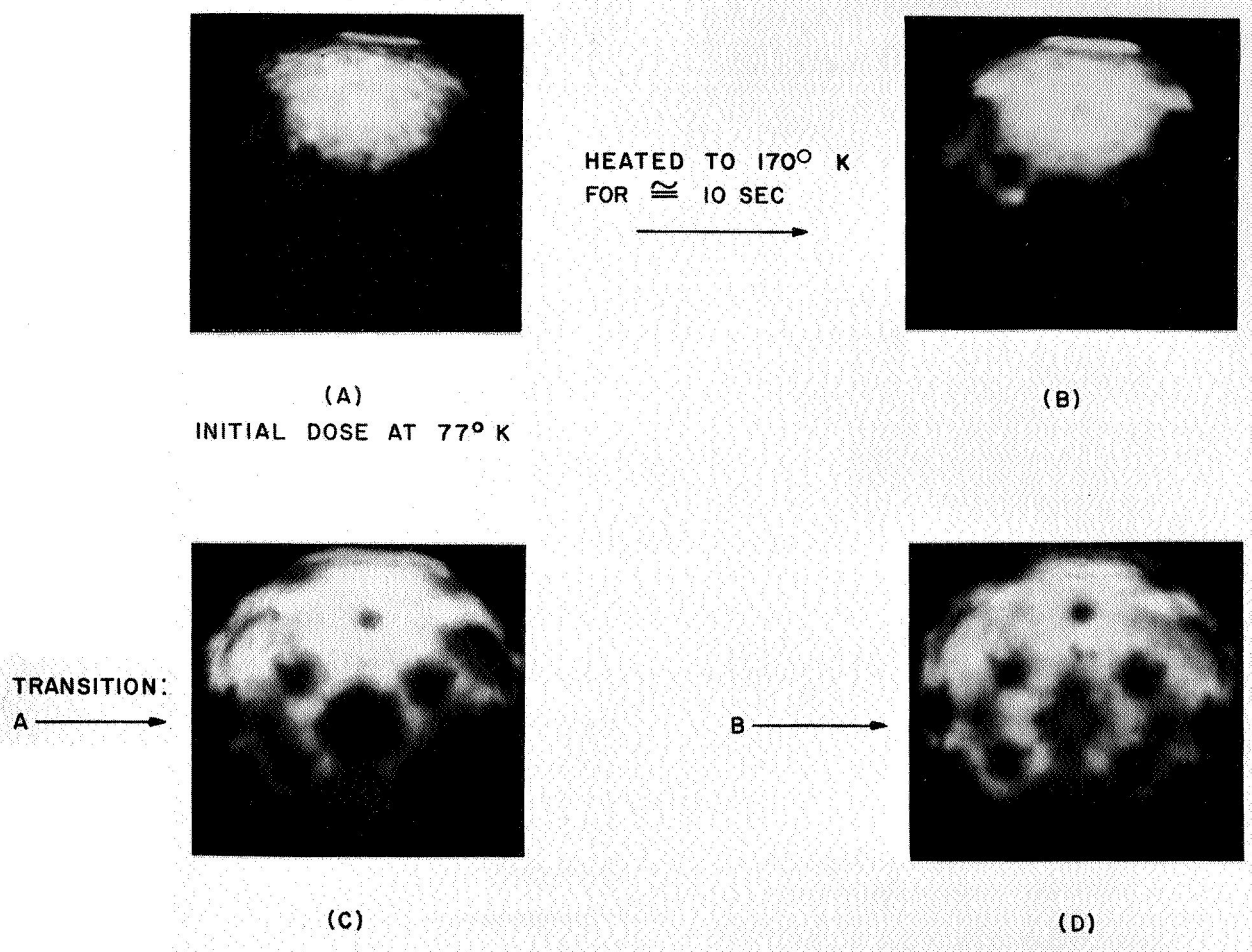


Figure 6. Surface diffusion sequence of cesium on (110)-oriented tungsten ($\theta_1 \sim 0.2$). Studies of the effect of field were made on the diffusion rates of the transitions between photo (B) and (C) (type A), and photo (C) and (D) (type B).

activation energy of surface diffusion E_d^F for the two modes were determined by assuming a diffusion coefficient D_F of the form

$$D_F = D_o \exp(-E_d^F/kT) = \frac{x^2}{t} \quad (24)$$

where D_o is a constant, and x is the distance traversed by the adsorbed Cs in time t . The temperature dependence of the diffusion rates in the presence of an electric field was found to obey Equation (24), thus permitting the calculation of E_d^F and D_o as a function of applied field. These results are given in Figure 7 for the two modes of diffusion investigated, where the distance x in Equation (24) was approximately 1500 Å, and the temperature range over which the measurements were made extended from 150 to 200° K. A similar dependence of both D_o and E_d^F has been reported for Ba on W.²³

The potential energy of an adsorbed atom diffusing over various atomically smooth crystallographic planes is generally regarded to imitate, to some degree, the physical surface; thus, a saddle and trough potential surface, as depicted in Figure 8(B) in one dimension, is expected to apply to a migrating adsorbed atom. The height of the barriers separating stable adsorption sites determine the activation energy for diffusion and varies with adsorbate, crystallographic plane, direction of migration, adsorbate concentration, and applied field. The variation of E_d^F with electric field was analyzed in terms of the field-dipole (μF) and field-induced dipole ($\frac{a}{2} F^2$) interactions. According to the model in Figure 8 (A), the effective field at the trough (F_t) and the saddle (F_s) positions differ from the field F for an ideally smooth surface of adsorbate according to $F_t = k_t F$ and $F_s = k_s F$. It is inferred from the model that $k_t < 1$ and $k_s > 1$. These considerations lead to an expression for the variation of E_d^F with F as follows

$$E_d^F = E_d^o - (k_s^2 - k_t^2) \frac{a}{2} F^2 - (k_s - k_t) \vec{\mu} \cdot \vec{F}, \quad (25)$$

where E_d^F is the activation energy with zero applied field. A least squares

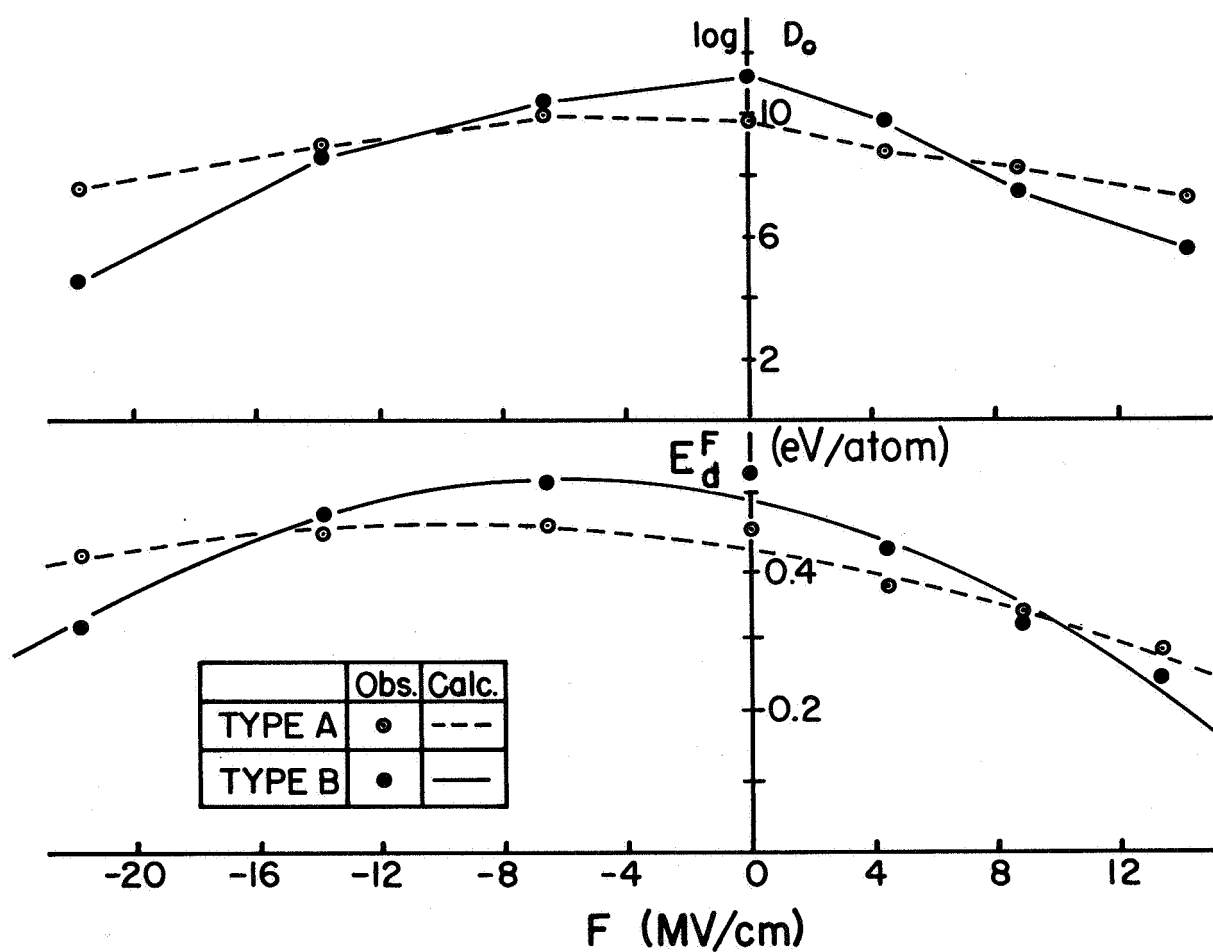


Figure 7. Surface diffusion activation energy E_d^F and logarithm of D_0 as functions of electric field F at the emitter surface for the two diffusion modes, type A and B. The curves are least square fits of Equation (25) to the data.

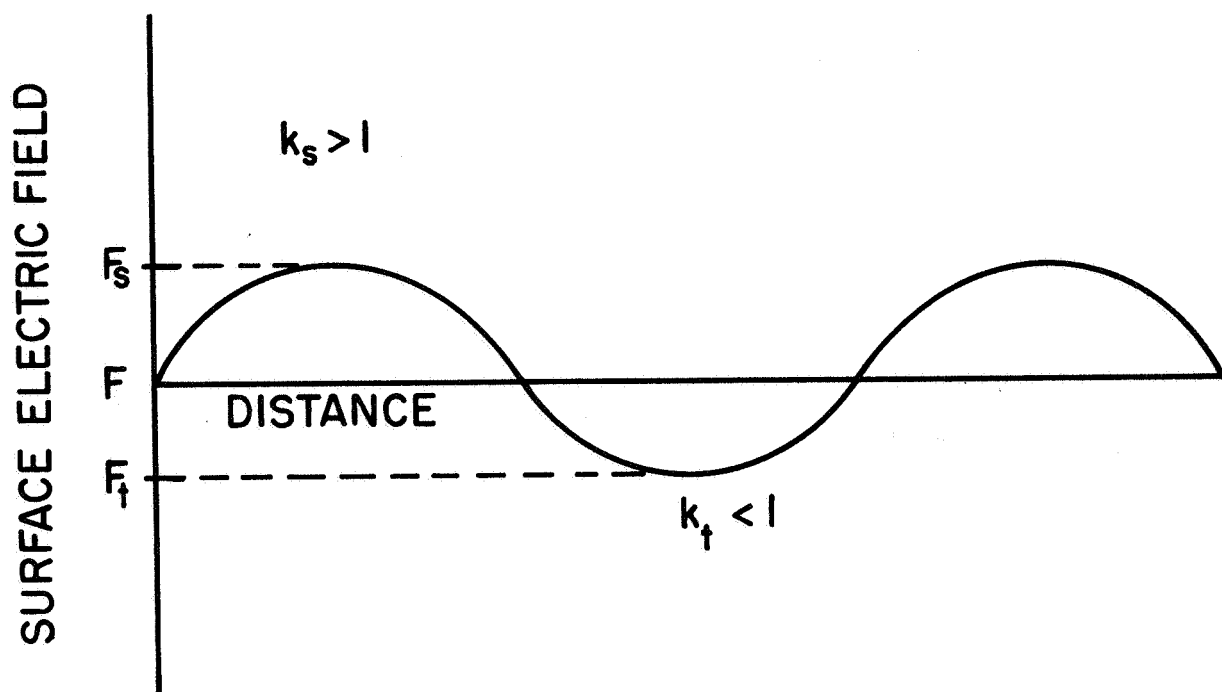


Figure 8(a). Variation of field with distance along one dimension of surface where F is the field at an ideally smooth surface, F_t the field on an ad-atom in the trough position, and F_s the field on an ad-atom migrating over the barrier between stable adsorption sites.

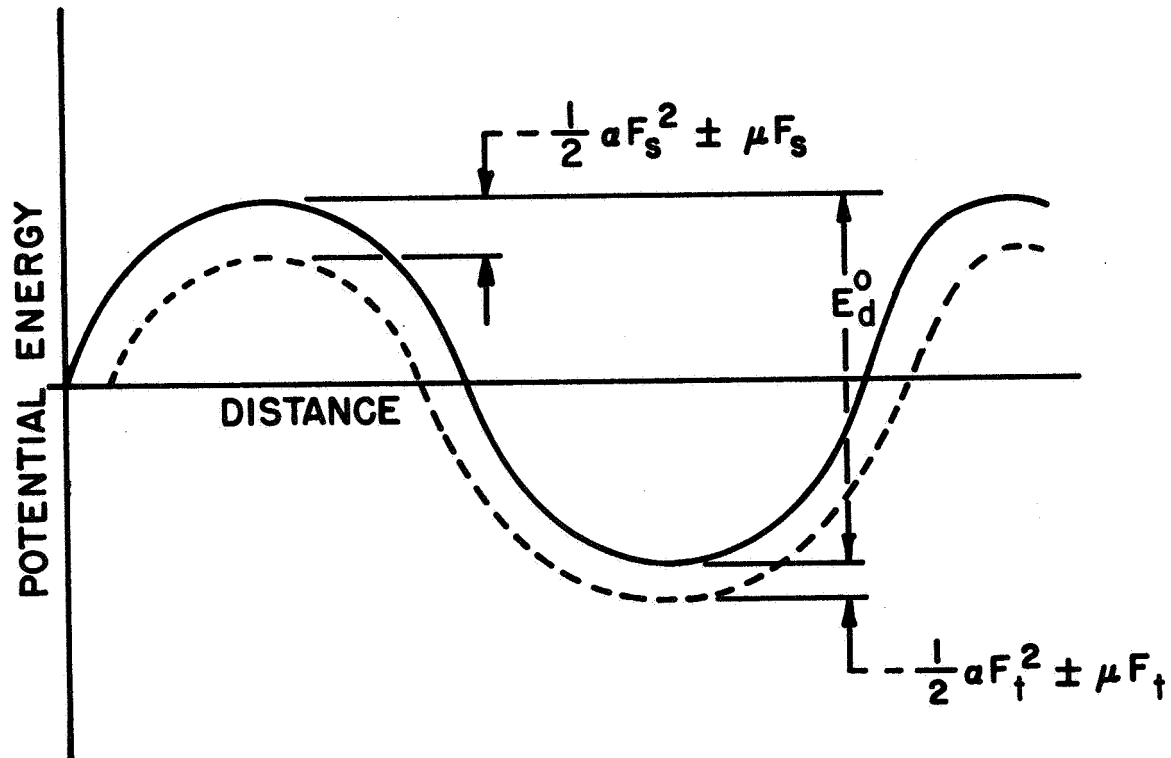


Figure 8(b). One dimensional variation of the surface potential energy of an ad-atom and the effect of field-dipole (μF) and field-induced dipole ($\frac{a}{2} F^2$) interactions on its shape.

analysis of the data for the two diffusion modes gives a reasonable fit to Equation (25) (see Figure 7), where the values of E_d^0 are 0.43 and 0.50 eV for type A and B modes respectively. It can also be shown that the coefficients of the F^2 and F terms of Equation (25) must be related to the field F_m corresponding to maximum activation energy as follows:

$$\vec{F}_m = \frac{\vec{\mu}}{a(k_s + k_t)} \quad (26)$$

The values of F_m are -9.93 and -5.88 Mv/cm for type A and B modes respectively. The negative values of F_m are in accordance with the negative dipole moments associated with the electro-positive adsorbate, and thereby lend support for this model. The smaller value of F_m for type B diffusion probably stems from a larger value of the field factor k_s , which would be expected if diffusion over (110) lattice steps is rate-determining for this mode.

Using a value of 8.4×10^{-18} esu for μ in this coverage range, we obtain from Equation (26) values of $a(k_s + k_t)$ which are 225 and 431 \AA^3 for type A and B diffusion respectively. It is doubtful from the model depicted that $(k_s + k_t)$ can exceed a value of 5, thus giving calculated values of a in the range of the known atomic polarizability. The reason for the pronounced variation of the pre-exponential factor D_0 with field, as shown in Figure 7, is not completely understood at this time. It has been speculated to arise from field-induced electronic transitions involved in the diffusion process²³ or entropy effects. An important consequence of the nature of the strong field dependence of D_0 is its compensation of the variations in D_F of Equation (24) caused by variations in E_d^F ; at high temperatures (e. g., 1000°K) the field dependency of D_F is determined primarily by the field dependency of D_0 rather than E_d^F .

THE CHARACTERIZATION OF BOND TYPES

In order to characterize the bond types occurring in surface adsorption it will be instructive to briefly summarize the general categories of surface bonds and their principal characteristics. Surface bonds can frequently be characterized in terms of electrostatic H^+ and nonelectrostatic H^n forces. In this context electrostatic interactions refer to a particle with a permanent charge or multipole moment interacting classically with its image inside the metal. Under nonelectrostatic binding forces one normally considers polarization and dispersion (or van der Waals) binding H_d^n in the case of physical adsorption, exchange or delocalization forces in the case of metallic binding H_m^n and localized orbital overlap in the case of covalent binding H_c^n . Each of these bond types contributing to H^n are enhanced by good adsorbate-substrate fit or by the maximization of nearest and next nearest substrate atoms. In contrast, electrostatic forces being longer range depend only weakly on substrate-adsorbate geometry but depend strongly on the local value of ϕ . In most cases, surface bonds involve simultaneous contributions from several of the above mentioned bond types, that is

$$H_a = H^+ + \sum_i H_i^n \quad (27)$$

where i refers to various nonelectrostatic forces involved in binding.

The bond type formed will depend on the electronic structure of the adsorbate and the value of $I_a - \phi$, where I_a is the adsorbate ionization potential. Small or negative values of $I_a - \phi$ favor large contributions from H^+ . For example, in the case of Ba/W²⁸ and Cs/W²² systems $I_a - \phi$ is small and $H_a = H^+ + H_m^n$; the H_m^n term is largest on low ϕ planes where adsorbate fit is usually good and the H^+ term is largest on the atomically smooth planes where ϕ is usually largest. This leads to a type of compensation which reduces the anisotropy in H_a with crystal direction². Adsorbates with large I_a , such as the inert gases, with filled outer electronic shells permit no electron exchange or covalent binding in the ground electronic state, hence for the most part, $H_a = H_d^n$ for inert gas adsorption. Systems for which $I_a - \phi \gg U$ (where U is the conduction

band width) and for which the adsorbate contains empty or partially filled levels at $-I_a$ are able to form localized "covalent" type bonds with some degree of ionic character.

Many of these expectations have been realized by experiment. In the Ba/W²⁸, K/W² and Cs/W¹ systems where H^+ is large, the high work function (110) planes exhibit the largest value of H_a . The inert gases,²⁹ on the other hand, are found to adsorb most strongly on the low work function atomically rough planes where H_d^n is maximized. For the CO/W system³⁰ adsorption also appears strongest on the atomically rough planes which maximize H_c^n .

For example, the basic difference between the Ba/W and Hg/W systems electronically speaking is the large value of $I_a - \phi$ which puts the filled 6s valence level of Hg well below the top of the conduction band of W; hence, donation of valence electronic charge to the substrate is prohibited in the first order unless empty surface states are available. Since this would lead to a positive rather than the observed negative dipole sign,³¹ it is more likely that the empty 6p level lies near the top of the conduction band and acts as an acceptor level undergoing electron exchange with conduction electrons. This type of interaction permits a net transfer of charge to the adsorbate (i. e., negative dipole moment) and maximizes the importance of overlap of relevant substrate and adsorbate orbitals and, hence, substrate-adsorbate fit. In other words, the primary interaction for the Hg/W system is $H_a - H_m^n$, whereas the Ba/W system contains a larger degree of electrostatic bonding.

In an attempt to further characterize the bond types we compare in Tables VII and VIII diffusion E_d and desorption E_a activation energies for several systems. The categorization of the E_d values according to actual crystallographic regions was accomplished by field emission microscopy patterns. Since in some cases more than one crystallographic region may be involved in the rate determining process, the region listed should be taken advisedly, particularly for the (110) diffusion.

There are several features in the Tables VII and VIII summarizations from

TABLE VII Summary of values of E_d and E_a for various systems.

	E_d (eV)				E_a (eV)
	(110) Regions	(111)	(123)	(100)	
Ba/W ²³	0.41		0.83		3.8
Cs/W ³³	0.48		0.76		3.3
Hg/W ³¹		0.51	0.40	1.0	1.92
CO/W ³⁴		1.44	0.89	1.48	3.9

E_a are terminal coverage values

Probably (221) planes contribute

TABLE VIII Ratios of E_d and E_a values for various systems and a comparison with calculations (values in parentheses) based on a Lennard-Jones type interaction with an internuclear distance of 2.83 Å.

	E_d^{110}/E_d^{123}	E_d^{111}/E_d^{100}	E_d^{123}/E_d^{100}	E_d^{110}/E_a	E_d^{100}/E_a
Ba/W	0.49 (0.53)			0.11 (0.13)	
Cs/W	0.63 (0.53)			0.15 (0.13)	
Hg/W		0.51 (1.16)	0.40 (0.53)		0.52 (0.37)
CO/W		0.97 (1.16)	0.60 (0.53)		0.38 (0.37)

which considerable insight concerning the bond type for the various systems can be ascertained. First, it is noteworthy to point out that structural anisotropies in E_d can be accounted for remarkably well by a pair-wise summation of a 6-12 Lennard-Jones interaction potential. The values in parenthesis in Table VIII are computer calculated values by Bacigalupi and Neustader³² for a 6-12 Lennard-Jones interaction potential between the adsorbed particle and substrate surface atoms where summations were carried out to 7 lattice distances from each adsorption site. The only adjustable parameter for obtaining the calculated values in Table VIII was the internuclear distance r_0 . Since the latter is poorly known, our approach was to find the value of r_0 for each system which best fit the Table VIII data. For all systems listed Table VIII the value $r_0 = 2.83 \text{ \AA}$ gave the best agreement with the experimental results. Detailed interpretation as to the implication of the r_0 value so obtained is somewhat dubious for this idealized model, although according to Table IX the only grouping of adsorbate electronic states that allows Cs, Ba and Hg to exhibit similar radii are the ionic states of Cs and Ba and the atomic state of Hg. An experimentally observed W/CO bond distance of 2.5 to 2.8 \AA obtained from earlier field desorption measurements³⁰ agrees remarkably well with the 2.83 \AA value obtained from fitting the 6-12 interaction to the Table VIII results.

It is from the values of E_d/E_a that the classification of the bond types becomes more apparent. The planes referred to in the E_d/E_a tabulations are those from which terminal desorption appears to take place. From the Table VIII results we note that values of E_d/E_a for the Hg/W and CO/W systems are considerably larger than those observed for the Ba/W and Cs/W systems. Large values of E_d/E_a are expected in surface bond types containing negligible electrostatic or ionic character such as the CO/W and apparently the Hg/W systems. This follows from the fact that the largest values of E_a for H^n type bonding occurs on atomically rough planes where E_d is large, whereas the converse is true for H^+ type bonding where the largest E_a values occur on the high work function, atomically smooth planes which, in turn, have the smallest E_d values. Although the 6-12 interaction is considered more appropriate

TABLE IX. Summary of ionic r^+ and atomic r_o radii³⁵; the W/CO bond distance is obtained from field desorption measurements.³⁰

	r^+ (Å)	r_o (Å)
Cs	1.65	2.60
Ba	1.53	2.15
Hg		1.50
W/CO		2.5 - 2.8

for dispersion forces (e.g., physical adsorption), it appears to hold equally well for the localized chemical bonding occurring in the CO/W system as shown in Table VIII.

The poor agreement in Table VIII between experiment and calculation for the Hg/W system can be reduced if it is assumed that a nearby higher index plane, such as the (411), is rate determining as far as diffusion of the boundary across the (100) plane is concerned. It would be difficult from visual observations of the emission patterns to distinguish between (100) or (411) diffusion. Thus, if the (411) is substituted for the (100) plane in Tables VII and VIII for the Hg/W system, the calculated values become: $E_d^{111}/E_d^{411} = 0.74$; $E_d^{123}/E_d^{411} = 0.34$; $E_d^{411}/E_a = 0.48$. These values agree more closely to the experimental values in Table VIII for the Hg/W results.

In view of the large contribution of H^+ to the binding in the Cs/W and Ba/W systems it is surprising that a simple 6-12 interaction, not only gives remarkable agreement between calculation and experiment for the E_d ratios but also for the ratios of E_d/E_a . If we assume, however, that the change in the longer range H^+ interaction is negligible compared to the variation in the shorter range H^n interactions as the atom migrates over the potential saddle during place change, it then becomes plausible for a 6-12 interaction to predict E_d ratios in spite of large electrostatic contributions. This can be illustrated by writing the potential energy H_a of a diffusing particle as

$$H_a = H^+(x, y, z) + H^n(x, y, z) \quad (28)$$

where the x, y , coordinates describe motion along the surface plane and the z coordinate describes motion normal to the surface. If during diffusion $dH^+/dz \ll dH^n/dz$, then the energy change in going to the activated state H_a^* is related to E_d as follows:

$$E_d = H_a^* - H_a = H^n(x, y, z)^* - H^n(x, y, z) \quad (29)$$

Thus, if the substrate motivated anisotropies in H^n can be adequately described by a 6-12 interaction as suggested by Schmidt²⁸ for the Ba/W

system, it follows that E_d ratios can be predicted by 6-12 interactions even for surface bonds with large electrostatic contributions.

The good agreement between calculated and experimental E_d/E_a ratios for the Ba/W and Cs/W systems, however, must be considered fortuitous. This can be seen by noting that $E_a = -H_a$ and combining Equations (28) and (29) to give

$$\frac{E_d}{E_a} = \frac{H^n(x, y, z)^* - H^n(x, y, z)}{-H^+(x, y, z) - H^n(x, y, z)} \quad (30)$$

from which it follows that only if the condition $H^+ \ll H^n$ holds, can E_d/E_a be independent of H^+ , in which case, Equation (30) becomes

$$\frac{E_d}{E_a} = 1 - \frac{H^n(x, y, z)^*}{H^n(x, y, z)} \quad (31)$$

To the extent that Equation (31) is valid, the values of E_d/E_a can be predicted from a pair-wise interaction such as the 6-12 potential. However, for the Cs/W and Ba/W systems the condition $H^+ \ll H^n$ is not met and hence we presume the rather good agreement between calculated and experimental values of E_d/E_a for the Ba/W and Cs/W systems is either fortuitous or stems from experimental values of E_d^{110} that are larger than reality due to weighting from (110) vicinals.

In summary we have shown that relative values of E_d can be adequately determined on systems with widely differing bond types from a simple 6-12 Lennard-Jones interaction potential. In addition, large values of E_d/E_a (where E_a and E_d relate to the region of terminal desorption) are indicative of a bond type containing a small degree of electrostatic bonding while the converse is true for systems with small ratios of E_d/E_a .

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